# REMOVAL OF SOME HEAVY METALS USING RESINS PREPARED BY FREE RADICAL POLYMERIZATION OF GRAFTED DATE-PALM-WOOD COPOLYMER WITH DIFFERENT VINYL MONOMERS

BY

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# *Dedication*

*I want to dedicate this work to my family especially my parents for their love, support and sacrifices, my KFUPM friends who made life with another taste and to my friends and relatives in Sudan for care, asking and support.*

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First of all I would like to thanks Allah who gave me strength, health and Patience to complete this work , I can't forget to thanks King Fahd University of Petroleum and Minerals for giving this opportunity to complete my Master's degree.

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| | | |
|---|---|---|
| **DPWF** | : | Date Palm Wood Fiber |
| **MA** | : | Methyl Acrylate |
| **AN** | : | Acrylonitrile |
| **FT-IR** | : | Fourier Transform Infra-red Spectroscopy |
| **SEM** | : | Scanning Electron Microscope |
| **PAN** | : | Poly Acrylonitrile |
| **DMF** | : | Dimethyl-formamide |

# ABSTRACT (ENGLISH)


Full Name : Nadir Mohammed Adam Osman

Thesis Title : Removal of some heavy metals using resins prepared by free radical polymerization of grafted date-palm-wood copolymer with different vinyl monomers

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In this work the copolymerization between date palm wood fibers (DPWF) and some vinyl monomers such as methyl acrylate (MA) and Acrylonitrile (AN) was done successfully using free radical polymerization, parameters of graft polymerization were studied and optimized such as reaction temperature, reaction period, concentration of initiator, volume of monomer and amount of catalyst to obtained the best yield of grafting. Characterization was done for the fiber and copolymer using (FT-IR) spectroscopy and (SEM) to confirm the completion of polymerization. The (MA) and (AN) grafted copolymers was treated by hydroxylamine hydrochloride in order to prepare poly-hydroxamic acid and poly-amidoxime chelating resins respectively, the formation of resins was confirmed using (FT-IR) spectroscopy. These resins were examined to remove heavy metals ions from aqueous solutions. Batch technique experiments were carried out using different resins dosages, initial concentration and contact time. Kinetics study was done for adsorption process of heavy metals ions onto chelating resins and it was show agreement with pseudo second order kinetic model also the intraparticle diffusion model was applied. Langmuir and Freundlich isotherms models were applied, and Langmuir isotherm model describe the adsorption process better than Freundlich one. Poly- hydroxamic acid resin was showed a better adsorption ability than poly-amidoxime resin towards Lead (II), Chromium (III) and Cadmium (II) metals ions.

# ABSTRACT (ARABIC)

# ملخص الرسالة

**الاسم الكامل**: نادر محمد آدم عثمان

**عنوان الرسالة:** إزالة بعض المعادن الثقيلة باستخدام راتنجات محضره من البلمرة المشتركه باستخدام طريقه الجذور الحره لخشب النخيل مع عده انواع من مونيمرات الفينيل

**التخصص:** كيمياء

**تاريخ الدرجة العلميه:** مايو,2015

في هذا العمل عمليه البلمره المطعمه المشتركه بين الياف خشب نخيل البلح وبعض منوميرات الفينيل مثل الميثيل اكريلات والاكريلونيتريل تمت بنجاح باستخدام طريقه البلمره باستخدام الجذور الحره, ايضا تمت دراسه كل عوامل البلمره المطعمه وتم ضبطها مثل درجه حراره التفاعل, زمن التفاعل, تركيز البادئ, حجم المونمر وكميه العامل الحفاز وذلك بغرض الحصول علي افضل عائد من عمليه التطعيم البولمري, عمليه توصيف الالياف والبوليمر الناتج تمت باستخدام جهاز مطيافيه الاشعه تحت الحمراء وجهاز مجهر المسح الالكتروني للتاكد من انتهاء عمليه البلمره. البوليمرات المشتركه بين الياف النخيل و الميثيل اكريلات او الاكيرلو نيتريل تمت معالجتها بواسطه الهيدروكسيل امين هيدروكلورايد من اجل تحضير البولي-هيدروكسميك اسيد والبولي-اميدواكسيم كراتنجات مخلبيه علي التوالي, تم التاكد من اكتمال عمليه تحويل البوليمر الي راتنجات مخلبيه عن طريق مطيافيه الاشعه تحت الحمراء. الراتنجات المخلبيه الناتجه تم اختبارها في عمليه ازاله ايونات المعادن الثقيله من المحاليل المائيه. تم استخدام تقنيه الدفعه باستخدام كميات مختلفه من الراتنجات وتراكيز بدائيه مختلفه من ايونات المعادن وايضا زمن الاتصال. دراسه حركيه التفاعل تمت لعمليه امتزاز ايونات المعادن الثقيله في الراتنج المخلبي واظهرت النتائج تتطابق واضح لنموذج الرتبه الثانيه الكاذبه, وايضا تمت تطبيق نموذج الانتشار خارج الجزيئات. ايضا تم تطبيق نماذج كل من لانجمور وفرندليش الايسوثيرميه ووجد ان نموذج لانجمور يمكنه وصف النتائج بصوره افضل من نموذج فريندليش. الراتنج المخلبي المحتوي علي بولي-هيدروكسيميك اسيد اظهر قدره علي الامتزاز افضل من الراتنج المحتوي علي بولي-اميدوكسيم تجاه ايونات معدن كل من الرصاص الثنائي والكروم الثلاثي والكاديوم الثنائي.

# CHAPTER 1

# INTRODUCTION

Several types of trees such as rubber, coconut and palm cover great plantation areas in the world. These trees are almost not included in forests resources estimation which concern in woody biomass. They are counted as agricultural crop and considered as non-forest tree. However, these resources can provide valuable raw material for many uses like wood manufacturing or materials for households and other industries.

Saudi Arabia is the home land of the Date Palm Tree. It represent as one of the oldest trees in the world with more than 10000 years of age. In 2006, 7 million tons that is a world production of dates and Saudi Arabia came in second place after Egypt in top ten countries in production of date which also including Algeria, Sudan, Oman, Libya, Iran, United Arab Emirates, Pakistan, and Tunisia. The common name of date tree or date palm tree is *"Phoenix dactylifera*", characterized by pinnate, an edible fruit in the form of a drupe with a thin, "feather-like" gray-green leaves, papery skin, and a single, long, narrow, hard seed. Date palm wood has many uses such as posts and rafters for huts, because it not very durable and it is lighter than coconut. Another uses for date palm tree is construction of aqueducts, bridges and parts of boats and dhows. Moreover the residues of tree is burnt for fuel [1]. Date palm contain chemically three major components which it cellulose, lignin and hemicellulose as well as other minor constituents such as protein and oil. [2]

Most of the wood fibers possess an attractive properties like a poor wettability and moisture content for some coating or adhesives are refer to the hydrophilic characteristic of wood. A wide range of chemical modifications has been carried out to improve these properties such as paint, stain and related coating. These modifications generally provide physical interaction with the wood substrate but do not provide permanent modification for wood surface. Chemical treatment through initiating of covalent bond with the hydroxyl groups even in external surface or in cell walls may gave best modification. [3]

The development of industrialization and human activities have significant role on the environment through the elimination of waste containing heavy metals which provide their ions in the aqueous solutions. These heavy metal have high toxicity and harmful to all types of living species, including human. Most heavy metals possess positive charges (cations). Examples of heavy metals include copper (Cu), nickel (Ni), chromium (Cr), mercury (Hg), arsenic (As), cadmium (Cd), and lead (Pb). There was not any possibility of degradation of Heavy metals because they are belong to the earth's crust natural components. In a small portions they enter in our body through many ways like air, drinking water and food. Several heavy metals (e.g. selenium, copper, and zinc) are fundamental to maintain the metabolism of our bodies as a trace element. However, it will be dangerous and poisonous in the case of increasing the concentrations of these metals. For example this poisoning could be due to contamination of drinking water especially that came through lead pipes and intake via the food chain also ambient air with high concentrations near emissions sources. [4] Removing heavy metals ions from water during the water treatment process has attracted much interest in order to environment protection and saving the health of the people. [5]

Classical methods was applied to remove heavy metals ions from wastewater solutions commonly involve precipitation by chemical reagent, ion exchange, evaporation methods, separation using membranes, and cementation electrolysis, etc. But from time to time, these methods of treatment didn't gave satisfying removal rates to face the control limits of pollution or are sometimes expensive. [6]

In order to satisfy and solve the above mentioned problems the world resort to Bio-sorption or sorption by material of biological origin appears due to their technically workable and cost-effective approach. Newly some natural materials such as cellulose, Chitosan, chitin, and their derivatives have been specified as an attractive option because of their economic efficiency, characteristic properties, safety, and biodegradability.

Ion exchange is a reaction in which free mobile ions of a solid are exchanged for different ions of identical charge in a solution. The exchanger must contain an open network structure, either organic or inorganic, which carries the ions and let ions to pass through it. Ion exchangers either organic or inorganic, are of natural or synthetic origins. The ones that are widely used nowadays are synthetic resins that function as ion exchangers because they are three-dimensional organic networks bearing charged or potentially charged groups. [7]

The main interest of using date palm fiber in this study is due to their abundant and renewable source here at the Kingdom of Saudi Arabia. At low cost. Moreover, the date palm fiber forms biodegradable materials when treated with certain monomers and can be obtained at low costs compared with the increasing costs of the plastics which are commonly used for the metal removal from water.

## 1.1 Statement of problem

Heavy metals contaminated water represents a major health and economic problem globally, particularly in the developing world. Metal contamination arises from a number of sources such as mining, industrial and urban wastes and is a problem which may be exacerbated through the use of contaminated water sources for drinking or irrigation. Existing technologies for metal remediation include ion exchange but may produce poor results, particularly if recovery of the metal ions is desired. Pollution divided onto two types, first one is point source which include solid discharge and effluents from vehicle exhaustion, industries, emission and metals discharged from mining and smelting. The second type is nonpoint sources which include natural and artificial soluble salts, disposal of domestic and industrial wastes in agriculture, as well as uses of pesticides or insecticides. Both type effect on animals plants as well as pepole health, but those that add heavy metals to water and soil are of serious concern because to their insistence in the environment and increasing the cancer rates. Heavy metals was not biodegradable it's just transform form oxidation state to another, therefor the effect of heavy metals on human health and environment attracted great attentions nowadays.

Most heavy metals ion such as Cu, Ni, Pb, Cd, Cr, As, Hg and Zn classified as environment pollutant the sources of these metals listed in the table (1.1). The concentration of particularly metal was different from source to another and depend on the source of it. The presence of heavy metals in plants may cause acute and chronic diseases and effect on human nutrition. For example, Zn and Cd can lead to respiratory and acute gastrointestinal also damages and acute heart, brain and kidney damages. [8]

**Table 1 Different sources of heavy metals.**

| Heavy metals | Sources |
|---|---|
| **As** | Petroleum industries, semi-conductors, wood preservatives, volcanoes, animal feed additives, herbicides, coal power plants, smelting and mining [9] |
| **Cu** | Mining, electroplating, smelting and refining. |
| **Cd** | Application of phosphate fertilizers, geogenic sources, , metal smelting and refining, fossil fuel burning, anthropogenic activities and sewage sludge [9] |
| **Cr** | Electroplating industry, sludge, solid waste, tanneries |
| **Pb** | Burning of gasoline contain lead, smelting and mining process, metalliferous ores, municipal sewage, paints and industrial wastes enriched in Pb. [10] |
| **Hg** | Caustic soda industries, volcano eruptions, burning forest, coal, peat and wood burning |
| **Ni** | Gas exchange and bubble bursting and in ocean, volcanic eruptions, forest fire, land fill, weathering of soils and geological materials |
| **Zn** | Smelting and refining, Electroplating process, bio-solids and mining. [9] |

## 1.2 Objective of the study

- To prepare a new grafted copolymer from the date palm wood with some vinyl monomers through free radical polymerization.
- To optimize the reaction conditions in order to produce the grafted copolymer.
- To characterize the prepared grafted copolymer using a variety of techniques such as: FTIR, SEM, etc.
- To convert the prepared grafted copolymer into ion exchanger resins.
- To characterize prepared ion exchanger using FT-IR spectroscopy.
- To study the removal of heavy metal ions from aqueous solution using prepared ion exchanger.
- Evaluation the performance by applying the kinetics order models and adsorption isotherm models such as Langmuir and Frundlich.

## 1.3 The significance of the study

The problem of the clean sources of drinking water attracted a great attention nowadays, in this study will develop new cheap materials for water treatment. Moreover we will focus in removal of heavy metals particularly (Lead (II), Chromium (III) and Cadmium (II)).

# CHAPTER 2

# LITERATURE REVIEW

Nowadays the chemical modification of natural fibers or polymers attracted great attention and that for availability of many types of monomers. One of the most used and potentially powerful method to provide essential modification in whole properties of natural polymers is grafting it's also retention of the desired specifications of fiber. [11]

Graft copolymerization is one of the most useable techniques for modifying the chemical and physical properties of a polymer. The demand of new materials with specific technological properties such as high strength, high modulus, toughness and low density, combined with positive and friendly impact in environment that lead to focusing in the lignocellulosic biomass of eternal and annual plants as raw material for the production of various new advanced polymeric materials. [12]

Cellulose classified as one of the oldest natural polymers. It has many properties like renewability, biodegradability also it can be modified to produce many beneficial products. It was fabricated by various plants as hair or as a structural polymer in cells. [13] The main source of cellulose is the wood it found as a texture combining with lignin, the production of wood and cellulose is sustainable which offer many ways for uses, many recent research paper study the modification of cellulose by combining with polar and ionisable groups and applications of new polymeric materials in industries such as petroleum, papermaking, textiles as well as environment protection. [14]

Some of vinyl monomers when it is a graft polymerized with cellulose was applied for separation of mercuric ions from neutral aqueous solutions in contain various transition metal ions. The sorbent is efficient and reaction was fast for that we can use for water treatment process even wastewater or drinking water. [15] The grafted coconut husk with AN was used to remove mercury(II) from aqueous solutions and wastewater produced from chloralkali industries [16], While banana leaves modified by adding functional groups like phosfosulfonate, sulfate and phosphate and used to remove heavy metals ions and the results show that the efficiency of removal increased after modifications.[17] Also a new chelating materials derived from sugarcane bagasse were prepared and used for metal ions adsorption from aqueous solutions.[18,19] methylene blue (MB), cadmium (II) and copper (II) were been removed using cheap solid adsorbent prepared from date pits. [20] Another low coast adsorbent prepared form wood sawdust which is a by-product of the world industries, and contain contain the texture of cellulose–lignin polymeric structure was used for removal of copper (II) and iron (III) under variable conditions after physical modification. [21] Also rice bran hemicelluloses have the potential for binding heavy metal ions. In addition, it was concluded that different chemically modified orange peel cellulose bio-sorbents possess an ability to adsorb some heavy metal ion effectively from aqueous solution. [22] Aspen wood fibers was examined for removal of copper (II) before and after modification of fibers, the sorption behavior using aspen fibers as natural adsorbents was studied. [23].

## 2.1 Date palm as adsorbent

Many research papers was conducted to study removing of heavy metals ion from water or waste water using data palm as natural adsorbent.

Al-Ghouti *et al*. (2010) study adsorption copper (II) and cadmium (II) using natural date pits as adsorbent without any modifications, they investigated adsorption capacities of the adsorbent and were found 35.9 mg/g for copper (II) and 39.5 mg/g for cadmium (II) by using Langmuir and Freundlich models, also they study the effect of pH, they assume heterogeneous surface binding that for fitting data with Freundlich model. [20] Date stone and palm tree wastes also were used in removal of $Cu^{2+}$ from aqueous solutions, this work was done by Belala *et al*. (2011). They were study the relation of between percentage of copper adsorption and size of the sorbent, particles with size blew 1.0mm gave the higher percentage of copper adsorption. Adsorption was fast maximum sorption capacity was gained within 20 min. The kinetics data was agreed with pseudo-second-order model and they suggested there was physical interaction between copper and solid sorbent. [24]

Date tree leaves were used as a natural sorbent to adsorb $Pb^{2+}$ from aqueous solutions, at low initial concentrations the percentage of removal was gave a maximum value. Many parameters were studied like "initial concentration" of $Pb^{2+}$, "contact time", pH, agitation speed and adsorbent dose. The optimum percentage of lead removal was obtained at pH 5.8 and 50 min while agitation speed and adsorbent dose were 50 rpm and 1.0 g/L respectively. The "Temkin model" describe the equilibrium data perfectly, sorption and kinetic data show good agreement with pseudo second order model, this work was done by F. Boudrahem *et al* (2011). [25]

Another study focus in adsorption of lead and Nickel using Iraqi palm date was carried out by Paul Ocheje and Raphael Odoh (2013), they were study different parameters, like temperature, pH, initial concentration, and contact time. They found that the extent of metal ions removed is less with higher contact time and became higher with increasing of initial

concentration. Langmuir adsorption model illustrate the kinetics data of this adsorption process clearly. [26]

## 2.2 Modified Date palm as adsorbent of heavy metals

The adsorption capacities of date pit activated carbons towards $Pb^{2+}$ and $Cd^{2+}$ has been investigated by El-Hendawy (2009), data was fitted with Langmuir model, the surface area of date pits activated carbons play significant role in increasing of adsorption capacity compare with raw date pits, the adsorption of lead somewhat higher amount than cadmium due to suitable pH for complexation or deposition and lower solubility. [27] Toxic chromium (VI) was been removed from different aqueous solution using adsorbent contain activated carbon form date palm seed using sulphuric acid activation method, this work was done by El Nemr *et al*. (2008). The degree of pH control on the percentage of adsorption the optimum pH was 1.0 and increasing of pH decrease the percentage of adsorption. 120.48 mg/g that is the maximum adsorption capacity chromium (VI) and the equilibrium was obtained in 180 min due to fast adsorption process. [28]

Abdulkarem and Al-Rub (2004) was studied the removal of Lead (II) onto activated carbons and 8-hydroxyquinolinemodified activated carbons was prepared from date pits. The adsorption capacity was high in both carbons. Moreover, there was no significant improvement in adsorption after modification. Removal of Pb (II) ions using activated carbons was increased with increasing of pH. This process followed "pseudo-second-order kinetics". "Langmuir and Freundlich models" showed good agreement from the equilibrium data for the process of adsorption of lead (II) ions. [29]

An activated Tunisian date stones treated with phosphoric acid as activation agent was used for removal of copper (II) from aqueous solution. The best activated carbon for removal

process obtained with 60% of phosphoric acid and impregnation ratio of 1.75 in 450 °C. Dubinin–Kaganer–Radushkevich and Langmuir adsorption isotherm models were enough to explain adsorption of copper (II) onto activated carbon. ($q_{\circ}$) was found to be 31.25 mg/g. F. Bouhamed (2012) et al suggested chemisorption process from kinetic data that were fitted with "pseudo-second order kinetic model". [30]

El-Said Ibrahim and Salma Muhammed (2013) were modified leaflets of date palm using sulphuric acid method at 170 ºC. They suggested that the hot sulphuric acid will dehydrate and give carbon with reduction property. It used to adsorb copper and silver from aqueous solutions, many parameters were studied such as contact time, pH, temperature and metal concentration from the results they found the adsorption of copper is fast compare with adsorption of silver it were reached equilibrium within ~2 h and ~60 h respectively. From the value of activation energy they suggested the adsorption of copper done throw diffusion-controlled ion exchange process, however the value of activation energy of silver indicate chemisorption of silver ions into carbon. [31]

Raw date pits was compare against $CO_2$-activated date pits in adsorption of copper and zinc ions. Banat et al. (2002) were found adsorption of both copper and zinc onto raw date pits is higher than adsorption onto activated date pits carbon and they attributed that to the difference in the surface functional groups of date pits and activated one. The heat involve from activation process may destroy the functional groups that were responsible for binding with zinc and copper. Also copper was showed better removal than zinc in both raw and activated date pits due to small ionic radius of copper and that provide an easy movement into pores surface. The best result was obtained in pH = 5 and temperature 25°C. [32]

## 2.3 Ion exchange resins uses for removal of heavy metals

Many research were conducted to study ion exchange processes in removal of heavy metal ions from even aqueous solutions or waste water due to their distinguished properties, such as high efficiency of removal, high capacity and fast kinetics [33], in both type of ion exchange resin even synthesized or natural the exchange process take a place through exchange resins cations with metals in the water, the synthesized resins were used more the natural ones. [34]

The resins containing acidic nature its most commonly used because it provide the acidic hydrogen easy to exchange with metals for example resins with sulfonic acid and carboxylic acid. Various parameters were effect on uptake of heavy metals ions such as "contact time, temperature, initial concentrations of metal" and pH. [35]

### 2.3.1 Ion exchange resin contain hydroxamic acid

Polymeric chelating resins functionalized by hydroxamic acid groups were attracted attention nowadays due to the complexion ability with wide range of heavy metals ions ,it was found act as chelating ligand with many ions like $Cr^{+3}$, $V^{+5}$, $Cd^{+2}$,$Au^{+3}$,$Pb^{+2}$ and other metals. The polymeric hydroxamic acid was synthesized by react of poly-(methyl acrylate) with hydroxylamine and this is basic reaction of preparation of hydroxamic acid, also there were many methods to prepare resins containing hydroxamic acid, moreover this resin had many applications.

Lutfor et al (2000) were synthesized a new chelating resin by reaction of poly-(methyl acrylate)-grafted sago starch with hydroxylamine and produced poly-(hydroxamic acid), they use free radical process to obtain the grafted copolymer then the ester group was treated with hydroxylamine and gave hydroxamic acid group. The product was fully

characterized using FTIR, TGA and DSC. Batch technique was used to examine the chelation behavior of the resin and it showed good result with chromium, nickel and copper. [36]

F. Vernon and T. Shah (1983) were studied the ability of Poly-(amidoxime)/poly-(hydroxamic acid) chelating resin to extract the uranium from sea water, they suggested the formation of tri-carbonato complex in the process of extraction. The resin showed high stability and fast sorption kinetics it can extract 12.5% of uranium in seawater within 2 seconds. [37]

Duolite ES 467 is another ion exchange resin functionalized by hydroxamic acid group, it was used for water treatment and removal of lead and iron ions, various parameter were studied. pH affected clearly on adsorption process increasing of pH was increase the sorption efficiency of lead but it will decrease for iron. This work was done by K Srinivasa et al (2005). [38]

A competitive study for extraction of gallium and vanadium from Bayer liquor using resin with a hydroxamic acid groups was carried out by K Srinivasa et al (2003). Alkali concentration and extraction time were most important parameters affected on extraction of both gallium and vanadium. Gallium extraction kinetics were fast than those of vanadium. [39]

### 2.3.2 Ion exchange resin contain Amidoxaime group

Many research papers were done to study the ability of amidoxaime chelating resins to adsorb heavy metals from even waste water or aqueous solution, the reasons of that is the complextion ability of those resins with various metal ions, also it provide electrostatic

forces, moreover the high stability of those complexes. Most of those papers focused in removal of toxic metals and extraction of inestimable metals.

A novel ion-exchange resin contain polyamidoxime group was synthesized by react grafted rubber-wood fiber with hydroxylamine this work was done by Faraj et al (2009). They suggested that the *syn*-hydroxyamino form was mainly the form of the cation-exchange resin. Also the study the water and hydrogen capacities of resin. The pH was studied in range 1-6 and chelating resin was showed an excellent adsorption capacity towards different metals especially copper it reached (3.83 mmol/g), also cadmium, iron, nickel, lead and cobalt. Column technique was used to separate cobalt and nickel from copper at pH = 3. The existing of amidoxaime group in polyacrylonitrile-g-rubber-wood fiber was confirmed using FTIR spectroscopy. [40]

Pinar and Olgun (2004) were used polymers with enriched amidoxime groups to remove heavy metals from concentrated solutions. They were used *N, N'*-dipropionitrile acrylamide monomer to prepare their adsorbents. Removal of various metals was studied such as $Cu^{+2}$, $Pb^{+2}$, $Co^{+2}$ and $UO_2^{+2}$ at high concentrations using batch technique. "Langmuir isotherm model" was used to confirm the interaction between $UO_2^{+2}$ and amidoximated groups. [41]

A novel poly-(acrylamidoxime) (CMC) chelating resin was prepared by double modification of Carboxymethyl-cellulose sodium salt, starting by grafting of Acrylonitrile onto (CMC), then the grafting product was converted to poly amidoxime chelating resin by treatment with hydroxylamine. Adsorption capacity for this toward bivalent metal ions was examined at different pH. Compare with other resins either synthetic or poly-saccharide based resins this resin showed competitive sorption capacity. [42]

Khalid et al (2008) were prepared Polyacrylonitrile (PAN) Nano fibers using electro-spinning technique, then they modified it with amidoxime group and used for metal ions sorption. They suggested that the adsorption of this new adsorbent followed Langmuir isotherm model, and monolayer adsorption was predominant in Nano fibers. Moreover this adsorbent showed high percentage of recovery it reached 90%. [43]

A composite chelating particles consist of poly-(amidoxime) and silicon dioxide was prepared by Baojiao et al (2010), they were study the properties of chelating adsorption and also investigated the mechanism of adsorption of heavy metal ions. From thermo dynamic data they suggested the adsorption process was endothermic chemical process, this adsorbent showed high efficiency for removal of copper and other metal ions such as nickel, lead and cadmium. [44]

# CHAPTRE 3

# EXPREMENTAL

## 3.1 Chemicals and materials

Date Palm fiber was obtained from local market with size less than 200 μm, fiber was washed tow times firstly with hot distilled water and then with acetone after that the water and acetone was removed by heating at oven in dried in 60 ◦C. Methyl acrylate (MA) and Acrylonitrile (AN) with high purity more than 99% were obtained from Merck's (Germany) and purified and activated by passing it through an activated alumina column to decrease the effect of inhibitor. Hydrogen peroxide as Analytical reagents grade was purchased from Sigma-Aldrich (USA). Ammonium ferrous sulphates, was used as received which is grade reagents was purchased from BDH (England). Acetone (Sigma-Aldrich) and N, N-dimethylformamide (DMF) (Fluka chemi). Sodium hydroxide and methanol (Merck). Hydroxylamine hydrochloride (Fluka).

## 3.2 Preparation of grafted copolymers

### 3.2.1 Graft Copolymerization of date palm wood fiber (DPWF) with Methyl Acrylate

Graft copolymerization was done in a two- necked round bottom flasks having a nitrogen gas inlet. Using oil bath with controlled temperature we added 100 ml of distilled water to the flask and stirring was started using magnetic stirrer. An amount of 1.0 g of the fiber was added to the flask and stirring continued to around 10 min. A quantity of 0.1 g of ferrous ammonium sulphate was added under nitrogen atmosphere while the temperature of the solution was kept at 90 $^{0}$C for a period of 15 min. A volume of 7.0 mL of the activated

methyl acrylate was added to the reaction mixture followed by a volume of 0.3 mL of 35% hydrogen peroxide with constant stirring. The temperature of the mixture was kept up at $90^0$C for a period of time of two hours. After reaction complete, the product was filtered after cooling the flask. The final product was washed with distilled water several times then dried using oven at a temperature of 60 $^{\circ}$C and left for overnight and weighed.

### 3.2.2 Removal of (MA) homopolymer and determination of graft level

Soxhlets extractor was used to purification of crude product and remove poly methyl acrylate homopolymer using acetone as solvent and purification was proceed for 24 h, the purified copolymer was dried at 70°C until constant weight, Eq. (3-1) was used to calculate the percentage of grafting (Pg).

$$P_g = \frac{w_2 - w_1}{w_1} \times 100 \qquad (3\text{-}1)$$

Where $w_1$ is the weights of the pure DPWF in grams, $w_2$ is the weight of the Copolymer after grafting and purification. [45]

### 3.2.3 Graft Copolymerization of date palm wood fiber (DWF) with Acrylonitrile

Graft copolymerization was carried out employing free-radicals methods using hydrogen peroxide as initiator with ferrous ammonium sulphate as co-catalyst. 1.0g of date palm fiber was placed into two neck round bottom flask with 100 ml of distilled water and 0.12g of ferrous ammonium sulphate was added to the flask and stirred for 15 min at 70 $^{o}$C under a nitrogen atmosphere. The nitrogen gas entering the reaction system was used to remove any oxygen present, to reduce the probability of formation of homo-polymer. 8ml of

Acrylonitrile (AN) was added and reaction mixture followed by a volume of 0.3 mL of 35% hydrogen peroxide, the mixture was stirred for 60 min., after that the sample was washed by distilled water several times after filtration, finally dried to constant weight in an oven at 70°C.

### 3.2.4 Removal of (AN) homopolymers and determination of graft level

The polyacrylonitrile homopolymer (PAN) was extracted with *N*,*N*-dimethylformamide (DMF) for 48h using Soxhlet extractor. The grafted copolymer was then dried at 65 °C in an oven for a day and weighed. The percentage of grafting (*Pg*) was determined using Eq.1. [3]

## 3.3 Preparation of ion exchange resins

20g of hydroxylamine hydrochloride ($NH_2OH$• HCl) was dissolved in 400 ml of a (methanol /water) solution (80%). Sodium hydroxide was used to neutralize the acidic content in hydroxylamine hydrochloride $NH_2OH$• HCl and the precipitated NaCl was filtered. This solution was added to the grafted product placed in a two-necked flask equipped with a condenser, and temperature was adapted using a thermostated water bath. The mixture was allowed to react at 70 C° under stirring for 180 min. After completion of the reaction, the resin was filtered and washed with the methanolic. The excess of Na OH in the resin was neutralized by treating the resin with a 0.1 M HCl solution for 20 min, then it was filtered again, washed several times with the methanolic solutions and then dried at 70 °C using oven until constant weight. [40, 46]

## 3.4 Characterization

The characterization of raw date palm fibre, grafted copolymers and ion exchange resins was carried out using various techniques which included: FT-IR which provide a useful information about functional groups in our compounds also this technique help to confirm the presence of new functional groups even in grafted copolymer or resin. Another technique used is "Scanning Electron Microscope" (SEM) it was used to investigate the morphology raw fibre surface before and after polymerization. Also we were used thermo-gravimetric analysis technique to study the thermal stability of the grafted copolymers and resins.

### 3.4.1 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR (Nicolet 6700 spectrometer- Thermo electron, USA) was provided by OMINC software, and deuterated triglycine sulphate (DTGS) as a detector. Samples were prepared using solid KBr pellet technique and spectra were obtained by using the transmittance mode with wave number over range between (4000 – 400 $cm^{-1}$), the number of scan was 16 and the background correction of background noise was done using resolution 25 $cm^{-1}$.

### 3.4.2 Scanning Electron Microscope (SEM)

The SEM photographs of the samples were taken using a "scanning electron microscope" model SEM 6400 (JEOL, Peabody, MA), and used to identify the morphology of the date palm fibre and grafted copolymers surfaces.

## 3.5 Sorption of heavy metal ions using the batch technique

Batch adsorption procedure was applied to study the equilibrium isotherms. A chelating resins were used within a solutions of different heavy metals in series of 125 ml plastic bottles and equilibrated with 20 ml of distilled water. After adding 20 ml of sodium acetate

(0.1 M) buffer solutions to the bottles, 10 ml of a 0.1 M heavy metals ions solution was then added. Various parameter were recorded, like effect of pH, effect initial concentrations, effect of contact time and effect of resin dosages in a range between (0. 5 – 2 g/L). Also temperature was been adjusted. A desired dose of resin was added to each bottle and shaked at 200 rpm at constant temperature until equilibrium was achieved. The metals ions adsorption at certain time, t, (qt mg/g) was calculated by this equation (3-2):

$$q_t = (c_0 - c_t) \times \frac{V}{m} \qquad (3\text{-}2)$$

Where "V is volume of heavy metal ions" solutions in liters, $C_0$ (mg/L) $C_t$ and (mg/L) are initial and final concentration at time t of heavy metals ions in solution, respectively and m (grams) is the weight of resin.

## 3.6 Data analysis

Various kinetic models "pseudo first order, pseudo second order and intra-particle diffusion" were applied to analyse the data that achieved from batch study at different resin dosage and concentrations of metal ions (70, 50, 30 ppm). The adsorption capacity of the resin was identify using different adsorption isotherm models (Langmuir isotherm and Freundlich isotherm). Also we use Atomic Absorption Specrtoscopy to measure the concentration of metals before and after the process of removal.

# CHAPTER 4

# Removal using Poly-(hydroxamic acid) Resin

## 4.1 Graft copolymerization

The reaction of graft copolymerization between methyl acrylate (MA) and DPWF was done by treating DPWF with initiator and cocatalyst solution ($H_2O_2$ and ferrous ammonium sulfate solution), this solution provide free radical sites in the backbone of DPWF. After that methyl acrylate (MA) was added to reaction and the formation of free radical sites from monomer particles was started. The copolymerizations process took place by forming covalent bond monomer and fiber radicals and create chain reaction for propagation. Also homopolymer of (MA) can occur due to presence of initiator in the reaction. Fig. (1) describe the mechanism of grafting. [3]

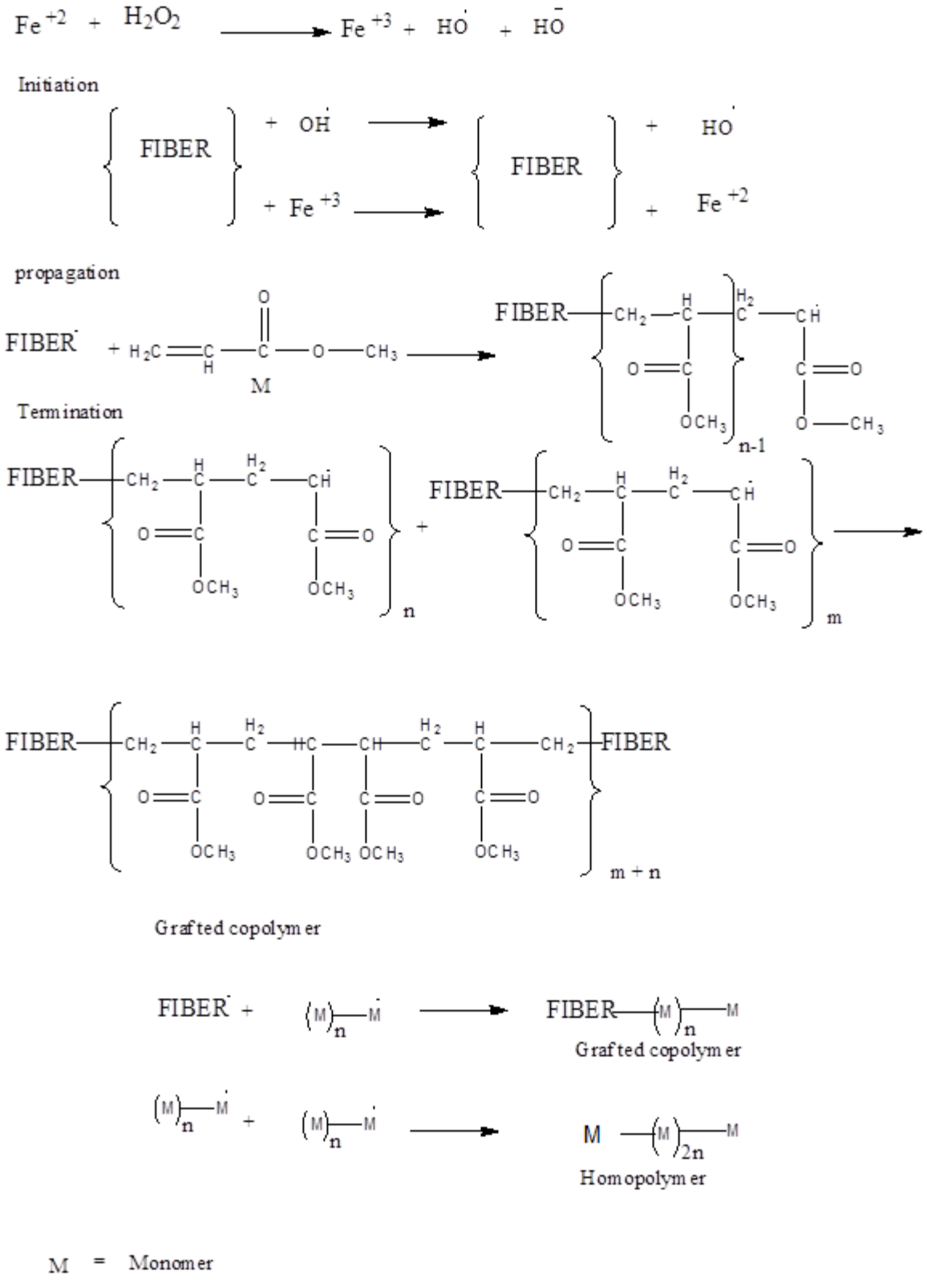



**Figure 1 Mechanism of graft copolymerization of MA onto DPWF.**

## 4.2 Optimization of grafted polymerization parameters

Different parameters were study to get the best conditions of graft polymerization such as temperature, time of reaction, monomer volume, cocatalyst amount and concentration of initiator, all these parameters were studied to give best yield of grafted copolymer product.

### 4.2.1 Effect of temperature

The temperature of the grafting reaction was studied in a wide range from 30 °C to 120 °C in this range of temperature the % yield of grafting increase gradually up to 90 °C it reach the maximum % yield of grafting after that it decrease with increasing in temperature. We can attributed this increasing of % yield of grafting with increasing of temperature to the swell-ability of DPWF onto substrate and the rate of diffusion of (MA) was enhanced to react with the active sites in the substrate with the increase of the temperature. Same observation was founded in the grafting of MA onto jute fibre [47] and MMA onto OPEFB [45]. To illustrate the decrease of % yield of grafting high temperature the main reason is the decomposition of hydrogen peroxide in high temperature that lead to producing many radicals and the chance to forming homoplymer increase. The data in Fig. (2) in agreement with the explanation.

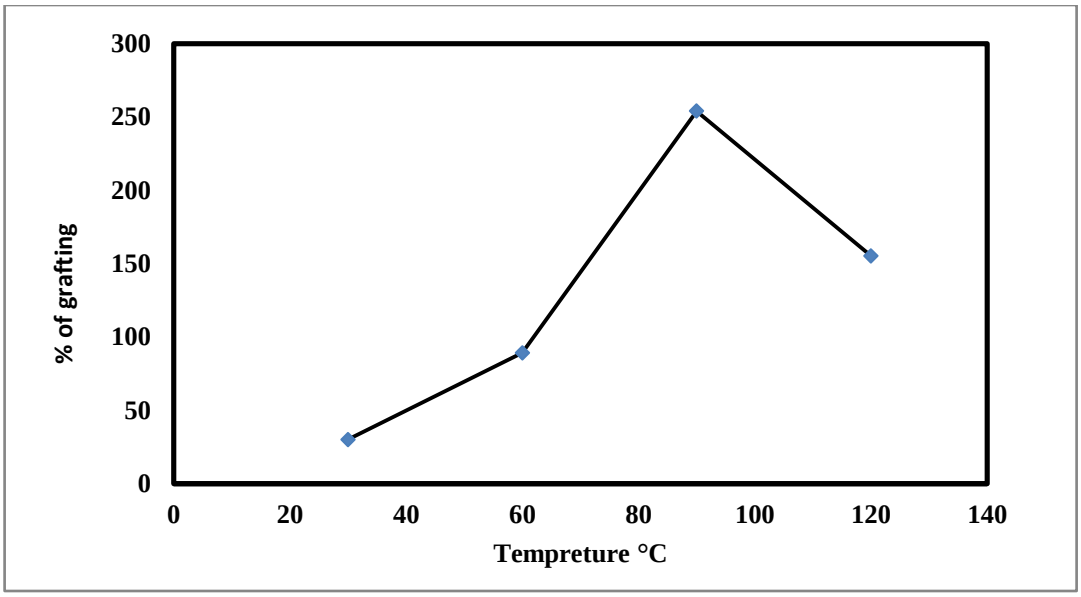



**Figure 2 Effect of reaction temperature on the % of grafting. Reaction time 120 min, MA 8 ml, $H_2O_2$ 0.03 M, $Fe^{+2}$ 0.01 mmol.**

### 4.2.2 Effect of the concentration of initiator

The % of grafting increase with increasing of concentration of initiator up to a certain limit and decrease after that as shown in Fig. (3). With the high concentration of initiator the production of radicals increase that lead to increase the number of the active sites in the backbone and that facilitate the grafting process. The grafting increase with increase of concentration of initiator from 0.01M to 0.03M and it decrease at higher concentration. The optimum % of grafting is152 at 0.03M of initiator. To explain the decrease of the % of grafting at high concentration of initiator, we found that high number of cellulosic fibre radicals will formed due to decomposition of initiator in high concentrations, the cellulosic fibre radicals may react with each other and terminate the reaction before the addition of

monomer. Also homopolymraization possible in high concentrations of initiator that will decrease the % of grafting. [48]

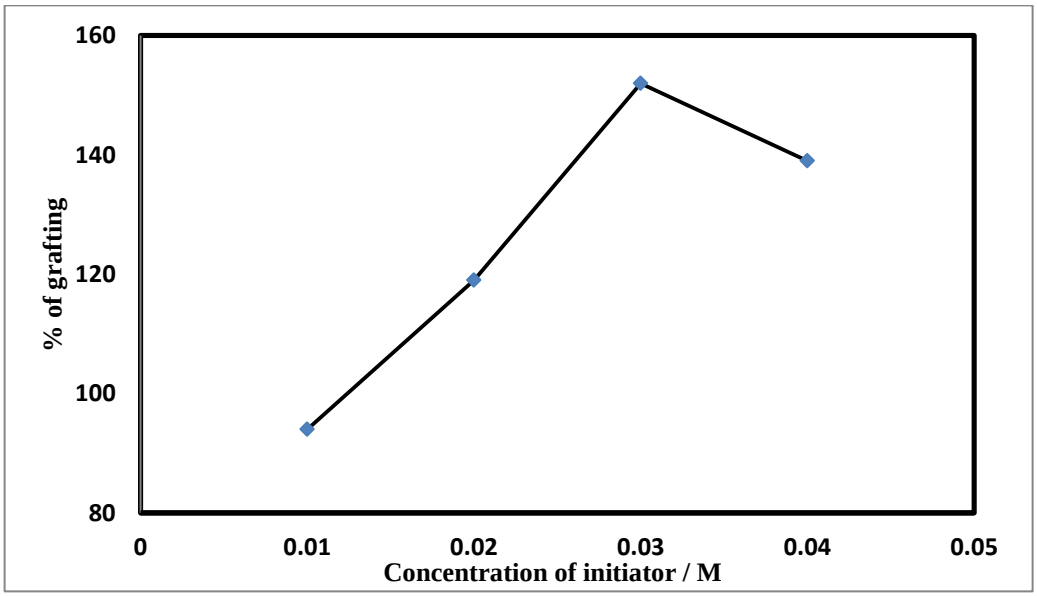



**Figure 3 Effect of the concentration of initiator $H_2O_2$ on the % of grafting. Reaction time 120 min , MA 8 ml, Temperature 90 °C, $Fe^{+2}$ 0.01 mmol.**

### 4.2.3 Effect of the amount of monomer

Increasing the volume of monomer (MA) from 2 to 8 ml will increase the % of grafting and then it will decrease with more volume of monomer (MA) as shown in Fig. (4). The optimum % of grafting is 189, at 8 ml of monomer (MA). We can attribute this increase to the abundance of the monomer that increased interaction with the active sites on the backbone. In the high volume of monomer the Probability of homopolymrization increase and that decrease the % of grafting.[48]


**Figure 4 Effect of the amount of monomer (MA) on the % of grafting. Reaction time 120 min, $H_2O_2$ 0.03 M, Temperature 90 °C, $Fe^{+2}$ 0.01 mmol.**

### 4.2.4 Effect of reaction period

The grafting reaction was done in a wide periods of time from 30 to 150 min .And Fig. (5) Explains that the % of grafting increase with time increase up to 120 min. After this time the % of grafting decrease. The reasons of this decreasing is that after this period the concentration of monomer , initiator and cocatlyst will decrease .Also all active sites in the backbone will be covered with the polymer , and homopolymerization is possible with long period of reaction . The optimum % of grafting is 152, at 120 min. [48, 67]

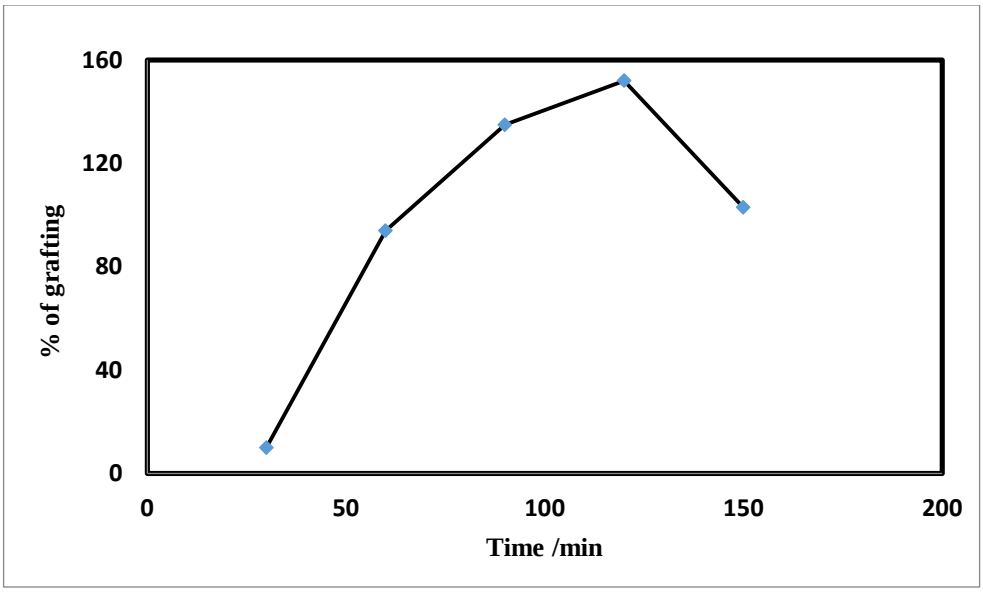



**Figure 5 Effect of reaction period on the % of grafting and efficiency. MA 8 ml, $H_2O_2$ 0.03 M, Temperature 90 °C, $Fe^{+2}$ 0.01 mmol.**

### 4.2.5 Effect of the amount of catalyst

The addition of a catalyst to the graft copolymerization reaction lead to increase in the % of grafting, but with the small amount of catalyst. As shown in Fig. (6) the optimum % of grafting is 206, at 0.15 mmol of catalyst "ammonium ferrous sulfate [$(NH_4)_2SO_4.FeSO_4.6H_2O$]", but the % of grafting decrease with increasing the amount of catalyst. The presence of catalyst in reaction speed up the process of hydrogen peroxide decomposition and formation radicals that increase the % of grafting , in high amount of catalyst a huge number of radicals will form and interact together and terminate the reaction that lead to decreasing of the % of grafting.[45]

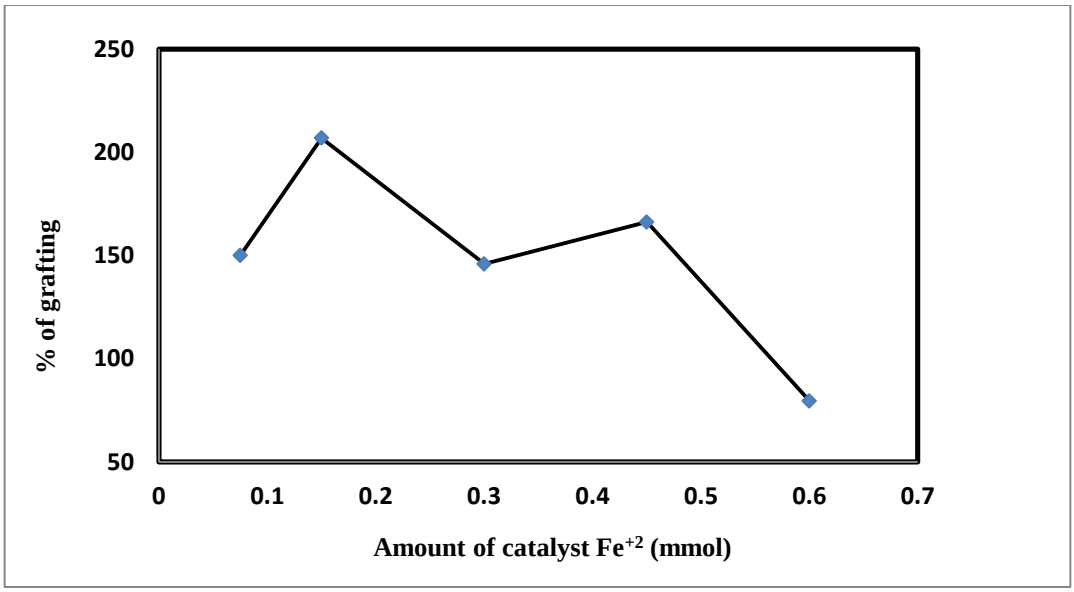



**Figure 6 Effect of the amount of catalyst $Fe^{+2}$on the % of grafting. MA 8 ml, $H_2O_2$ 0.03 M, Temperature 90 °C, 120 min.**

## 4.3 Preparation of poly-(hydroxamic acid) resin

The reaction of ester group in copolymer with hydroxylamine in an alkaline medium is a general method to prepare hydroxamic acid. The same ratio of PMA-grafted-DPWF and hydroxylamine was used in alkaline media, the temperature of reaction was 70 °C, the reaction was carried out for 180 min in a methanolic solution (methanol/water ratio = 80). The proposed a mechanism for the reaction between hydroxylamine and poly acrylate ester to give Poly - (hydroxamic acid) showed in Fig. (7). [49, 50]

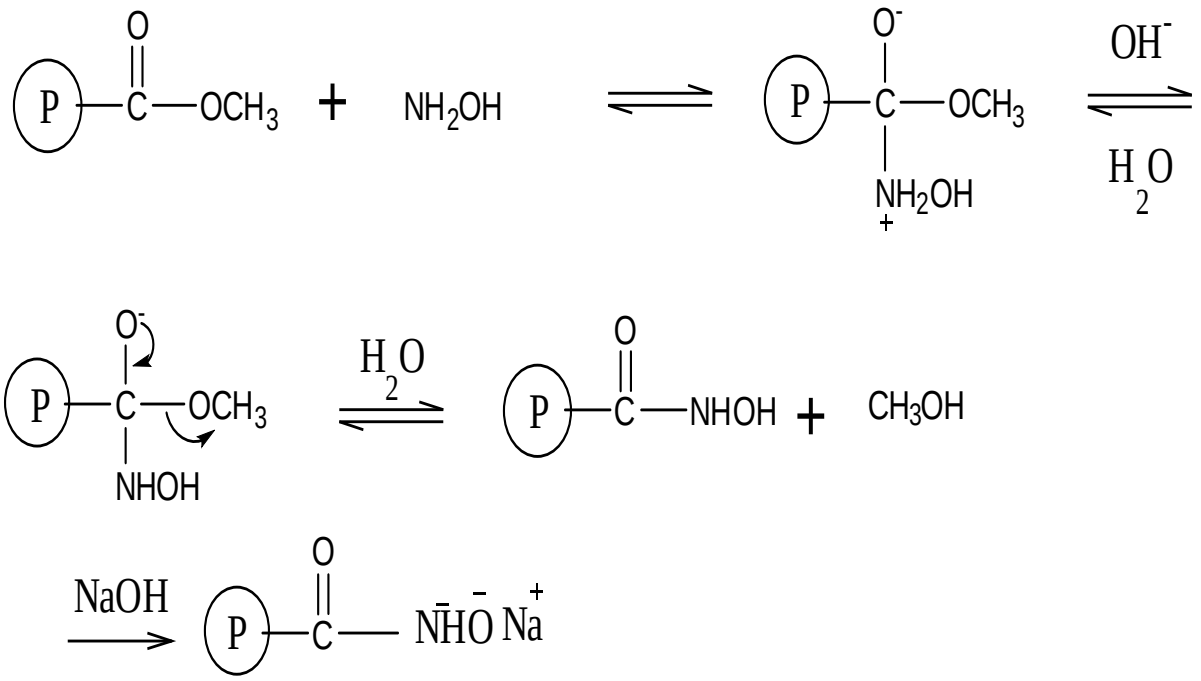


**Figure 7 Reaction mechanism of preparation of poly-(hydroxamic acid).**

## 4.4 Characterization of DPWF, grafted copolymer and resin

To characterize and verify the presence of poly methyl acrylate (PMA) on the DPWF fibre and presence of hydroxamic acid group we were using IR spectroscopy, Fig. (8) show the FTIR spectra for DPWF fibre, PMA-grafted-DPWF fibre and resin containing hydroxamic acid groups. In the range between 3100- 3500 $cm^{-1}$ a very distinguished broad absorption band assigned to hydroxyl group appears in all spectra, we can refer this to O-H stretching vibrations of absorbed water, celluloses, lignin constituent of DPWF and hemicelluloses. A small peak around 1740 $cm^{-1}$ in the spectra of DPWF could be assigned to carbonyl stretching vibration of carboxyl groups in lignin and hemicelluloses in DPWF, A sharp increasing in intensity of same peak at (1740 $cm^{-1)}$ in the spectra of PMA-grafted-DPWF could confirm the presence of an ester group from (MA) and that is clear evidence of grafting .[45] The C= O bands at1740 $cm^{-1}$ was shifted to form a new band

associated to carbonyl in hydroxamic acid (C= O at 1647 $cm^{-1}$) we can see that clearly in the spectrum of resin containing hydroxamic acid group.[50] Many absorption bands occur in both spectra such as the band in the 1400 -1600 $cm^{-1}$ were associated to the finger print area of aromaticity or benzene rings in lignin. Also the band in the region of 1000 – 1300 $cm^{-1}$ assigned to C – O stretching vibration of aliphatic alcohols in hemicelluloses, cellulose, and aromatic primary and secondary alcohol in lignin. [3, 45]

Another technique to confirm the grafting of DPWF fiber is SEM, figs. (9) and (10) show the micrograms of the DPWF fiber and PMA-grafted-DPWF fibre respectively, fig. (9) show the surface of the DPW before grafting, we can see the pores clearly on the surface .After grafting the surface is fully covered by PMA and it's homogeneous because it's chemically bonded as we see in fig. (10).

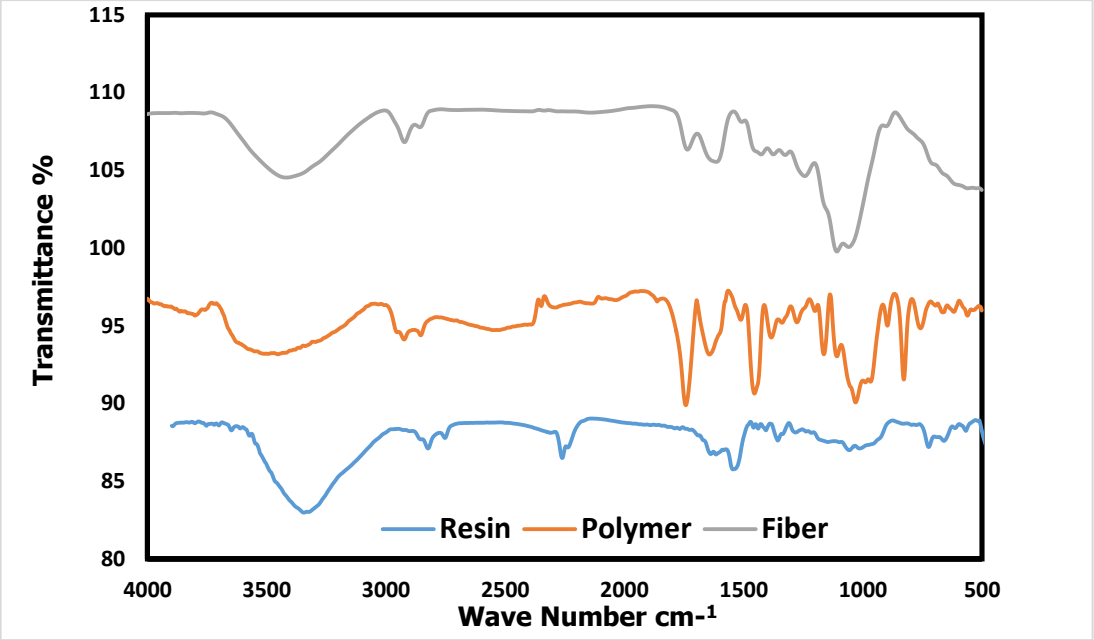



**Figure 8 FTIR DPW fiber (top- gray), PMA-g-DPWF fiber (middle - orange) and resin containing hydroxamic acid groups (Bottom - blue).**

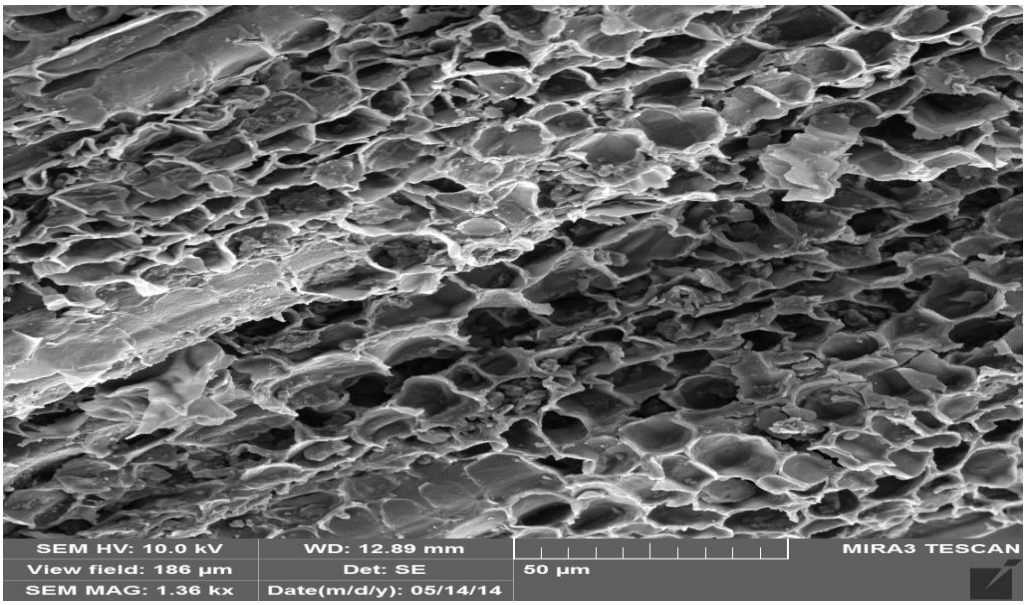



**Figure 9 Scanning electron micrographs of DPWF before grafting, SEM MAG. (1.36 KX)**

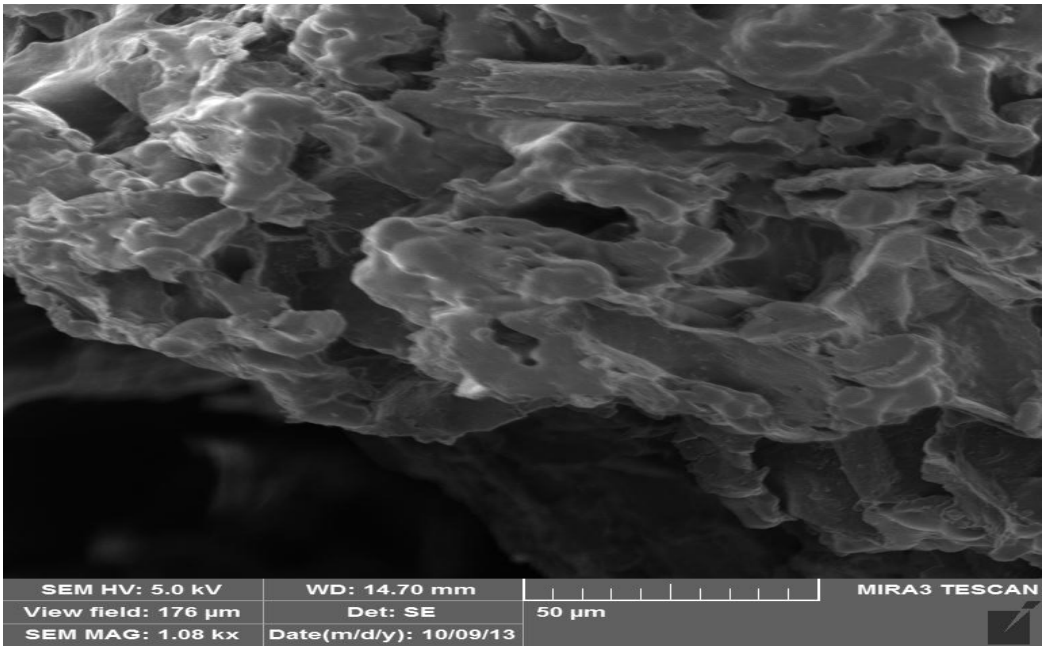



**Figure 10 Scanning electron micrographs of DPWF after grafting, SEM MAG. (1.08 KX)**

## 4.5 Effect of initial pH

The solution pH is a significant parameter in studying removal of heavy metal ions from water or aqueous solution due to many reasons such as affects in concentration of counter ion placed in adsorbent functional groups also the solubility of metal ions and the, addition to the degree of ionization of the adsorbate during the reaction [51]. In this work lead (II), Cr (III) and Cd (II) adsorptions were carried out in wide range of pH from 1.0 to 6.0 using a constant Cleating resin dose of 1.0 g and metals ions concentrations was s 50.0 mg/L at 25 °C. The results are provide in Fig. (11) the adsorptions of lead (II), Cr (III) and Cd (II) was maximum in the pH-range 5.0 to 6.0.

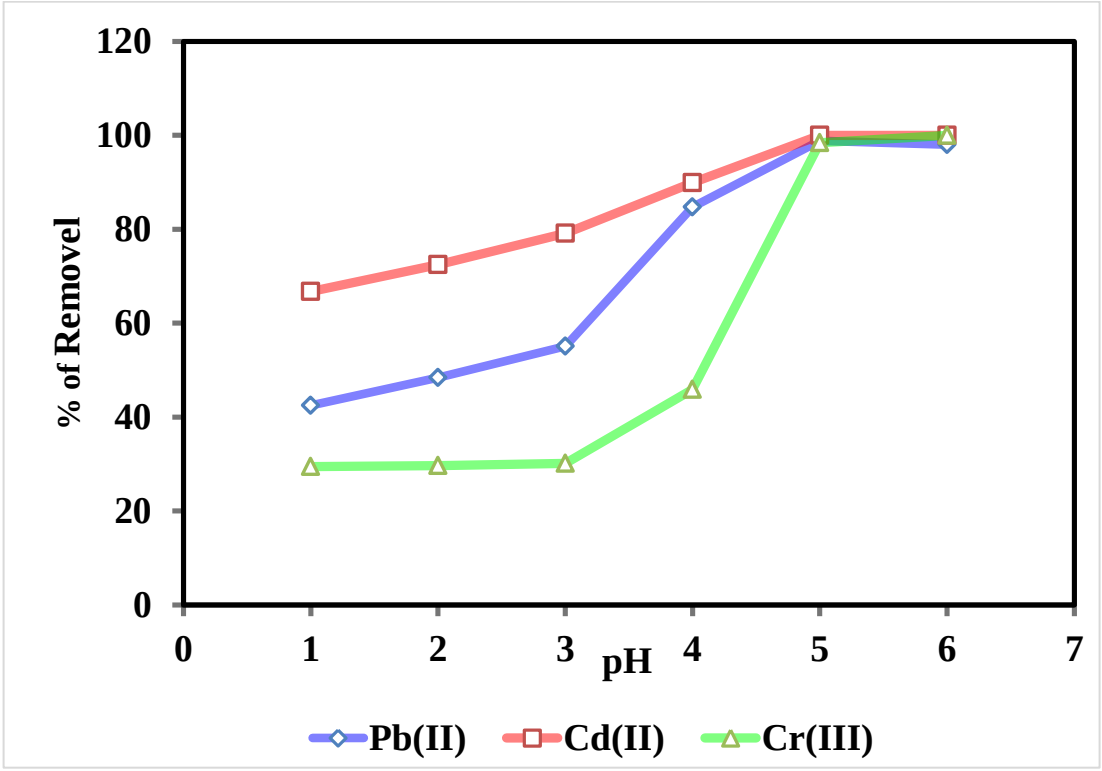
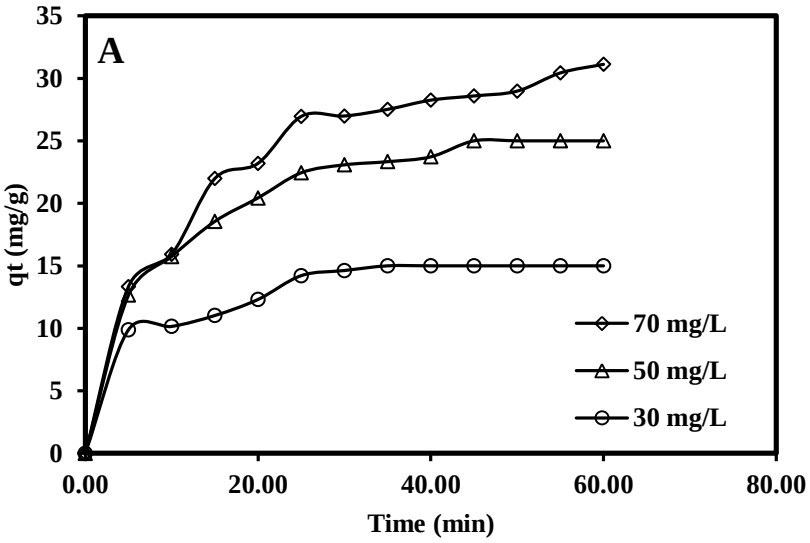



**Figure 11 Effect of pH on the adsorption of ($Pb^{+2}$) ($Cr^{+3}$) and ($Cd^{+2}$) ions, dosage of chelating resin 1g ions concentration 50 mg/L, time 60 min, and temperature 25 °C.**

## 4.6 Effect of contact time and initial concentration

Figure (12) illustrates the effect of contact time in adsorption of heavy metals from aqueous solution using Chelating resin at different initial concentration (30, 50and 70 mg/L), proper pH, and temperature (25 °C). We can see clearly that the increasing of contact time lead to increase adsorption of heavy metals also we can realize the adsorption is fast in the first 20 min and then gradually decreased to become constant after the equilibrium point. Also we can see the saturation point is almost reached at 40 min at all concentrations. [51] The presence of the active sites and uncovered surface on the adsorbent made the adsorption of metals ions very fast at initial stages.[2,52] The equilibrium time also effected by the nature and density of the adsorbent. Removal of lead (II), Cr (III) and Cd (II) dependent basically upon the initial concentrations. The amount of metal ions adsorbed, $q_t$ (milligrams per gram), increased by increasing in initial concentrations. For example at equilibrium the adsorbed amount onto Cleating resin increased from 15.00 to 27.97 mg/g, when the % of removal decreased from 100.00 to 79.91 % with the increasing in the initial Cr (III) ion concentration from 30 to 70 mg/L. we suggested that the ratio of available surfaces to initial metal ions concentrations was larger at low concentrations, on the other hand when we use higher concentration, this ratio was less and that confirm dependency of percentage of removal upon the initial concentrations. Also from the curve, we can indicate that the saturation which happened may increase the possibility of monolayer coverage of metal ions on the of Chelating resin surface. [53]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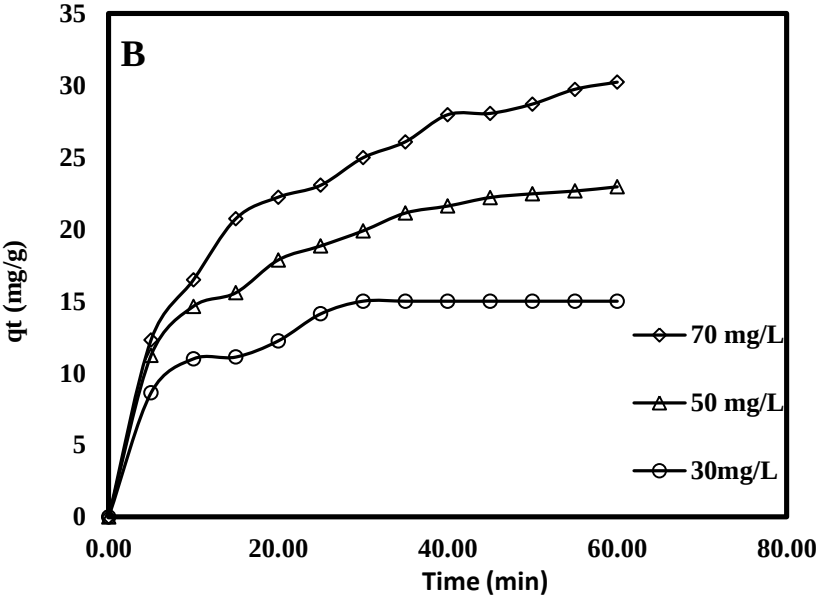
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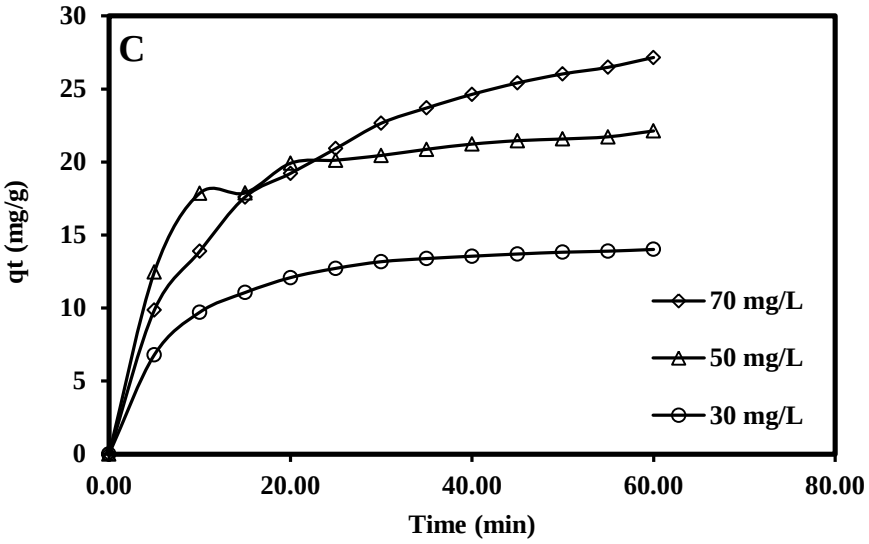



**Figure 12 Effect of contact time on (A) lead (II), (B) Cr (III) and (C) Cd (II) adsorption at different initial feed concentration, solution pH 5.5, and temperature 25 °C.**

## 4.7 Effect of adsorbent dosage

An important parameter that determine the efficiency of the adsorbents for a given initial concentration is the adsorbent dosage .Fig.(13) explain The effect of cleating resin dose on the adsorption of lead (II), Cr (III) and Cd (II), different dosages of chelating resin were applied for 50 mg/L at 25 °C. We find that the percentage of removal increased from 67.56 to 100% for lead (II), from 67.24 % to 100.00 % for Cr (III) and from 50.26 to 100% for Cd (II) with an increase of chelating resin dose from 0.05 g/L to 0.2g/L. We can refer that to the availability of the huge surface area due to increase of the mass of adsorbent or increasing of adsorption sites for constant concentration of metal ions. [52, 54] The percentage removal of heavy metals ions calculated using equation (4.1).

$$\% \text{ of Removal} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (4.1)$$

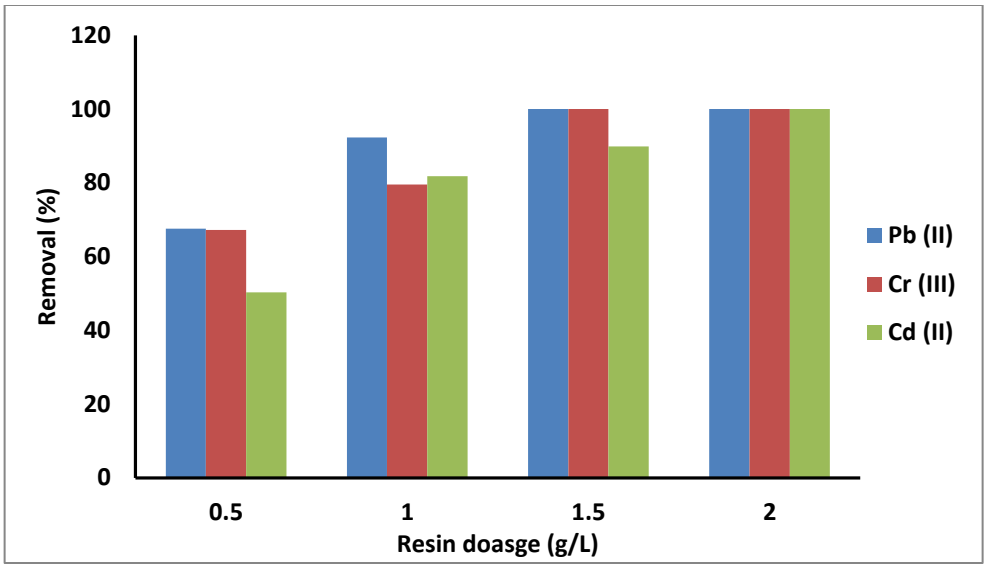



**Figure 13 Effect of adsorbent dosage on adsorption of lead (II), Cr (III) and Cd (II), initial concentrations 50 mg/L, time 60 min, solution pH 5.5, and temperature 25 °C.**

## 4.8 Adsorption kinetics

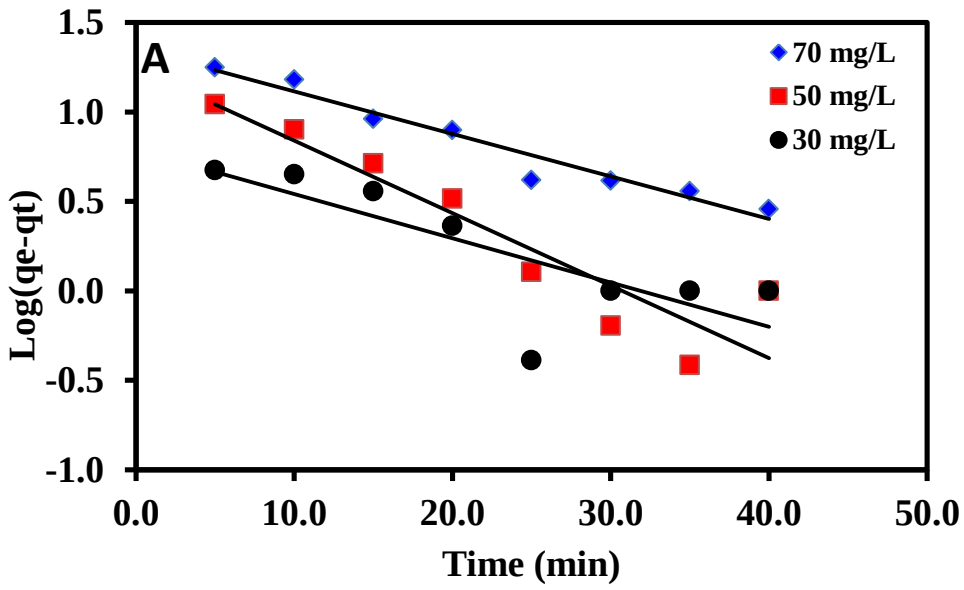
Adsorption kinetics explain the rate of solute uptake at interface between solid and solution and clearly provide important information about pathways and mechanisms of the reaction. [55] The kinetics of lead (II), Cr (III) and Cd (II) adsorptions on chelating resin was analysed using "pseudo first- order, pseudo-second-order and intraparticle diffusion models". The agreement between experimental values and the models predicted values was indicated by the "correlation coefficients ($R^2$)". A comparatively high $R^2$ values means that the models successfully describe the kinetics of metal ions adsorption.

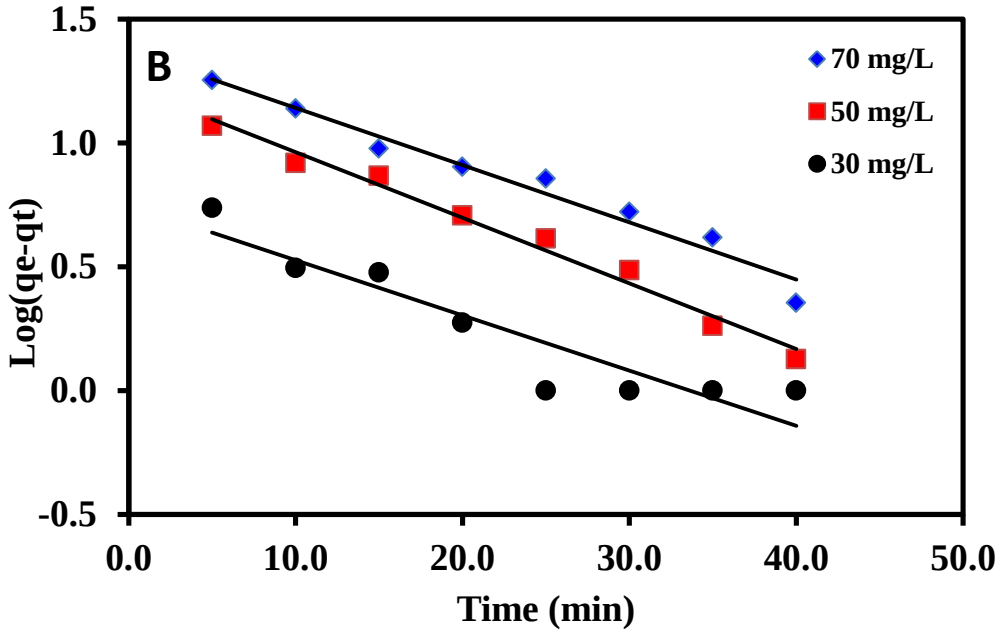
### 4.8.1 The pseudo-first-order model

The "pseudo-first-order equation", described in solid–liquid systems, is generally expressed as:

$$\mathrm{Log}(q_e - q_t) = \mathrm{Log}\, q_e - \frac{k_1\, t}{2.303} \qquad (4.2)$$

Where $q_t$ and $q_e$ are the amounts of metal ions adsorbed (milligrams per gram) at time t, and at equilibrium, respectively, and $k_1$ is the rate constant of "pseudo-first-order" adsorption (per minute).Fig. (14) illustrates the linearized form of the "pseudo-first-order model" for the adsorption of lead (II), Cr (III) and Cd (II)ions onto chelating resin at various initial concentrations , the values of rate constant $K_1$ and adsorption density $q_e$ were calculated from the slopes and intercepts respectively of the plots of log $(q_e - q_t)$ versus t ( Table 2). We realise from the low values of "The correlation coefficients ($R^2$) for the pseudo-first-order kinetic model" obtained at all the concentrations under study , and the bad quality of linearization ,beside the poor agreement between the experimentally observed equilibrium adsorption ($q_e$, exp) and that derived theoretically ($q_e$, cal) using Eq. (4.2). All these indicates that the adsorption of metal ions swerved frequently from the "pseudo-first-order kinetic model" and it failed to illustrate the adsorptions mechanism of metal ions on using chelating resin. [56]





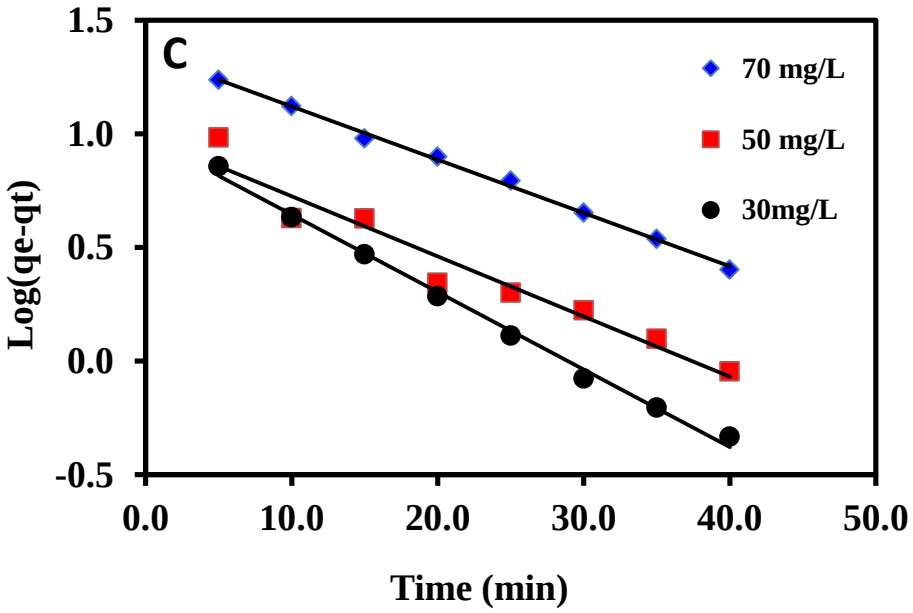




**Figure 14 Lagergren first-order plot for adsorption of (A) Pb (II), (B) Cr (III), and (C) Cd (II) on a Chelating resin for different initial feed concentration at pH 5.5 and temperature 25 °C.**

### 4.8.2 The pseudo-second-order equation

We investigate the "pseudo-second-order" adsorption kinetic rate using this equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4.3)$$

Where $q_e$ and $q_t$ are the adsorption capacities at equilibrium and time t (milligrams per gram), respectively, $k_2$ is the rate constant of the "pseudo-second-order" sorption (grams per milligram per minute). [57, 58] For the boundary conditions t = 0 to t = t and $q_t$ = 0 to $q_t$ = $q_t$, the integrated form of Eq. (4.4) will be as:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (4.4)$$

Which is the integrated rate law for a "pseudo-second-order" reaction. By make some rearrangement for Eq. (4.4) we obtained Eq. (4.5), which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4.5)$$

The initial adsorption rate, *h* (milligrams per gram per minute) is given as:

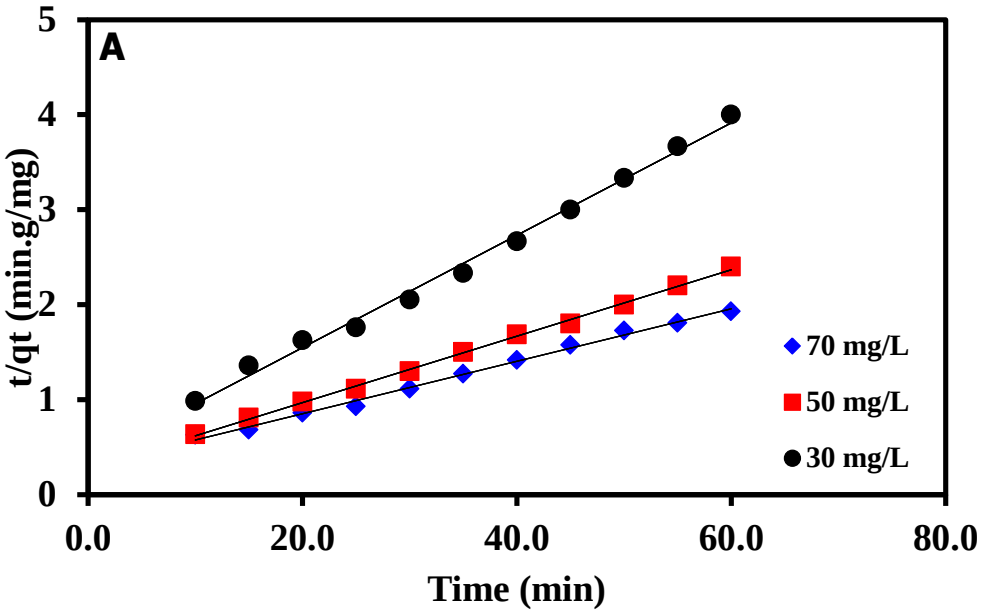
$$h = k_2 \ q_e^2 \quad (4.6)$$

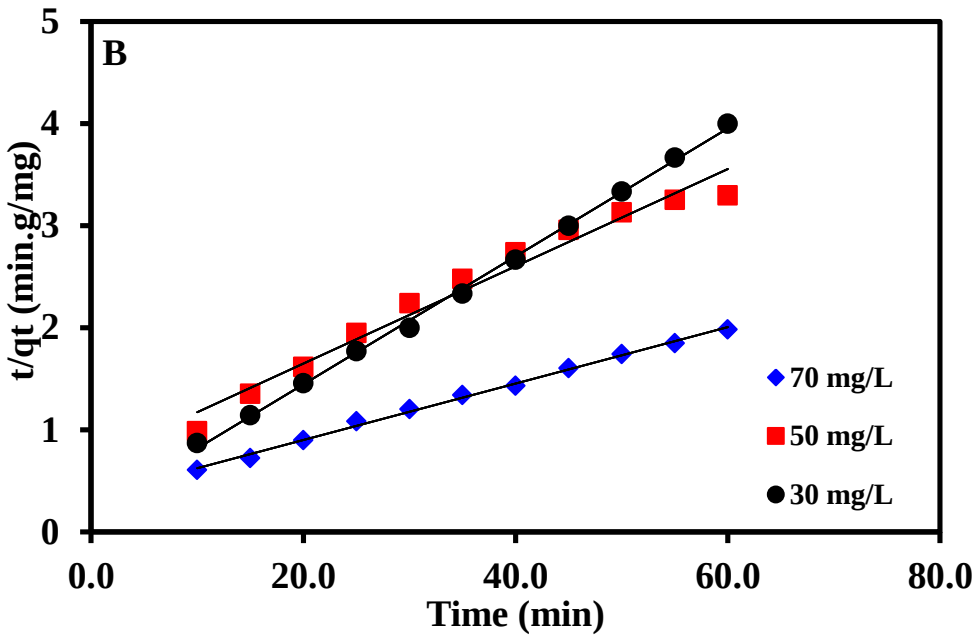
Eq. 4.5 also can be written as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (4.7)$$

From Eq. (4.4) the plot of $t/q_t$ versus t gave a linear plot Fig. (15). the value of $q_e$ (Cal.) and $k_2$ which are adsorption parameters were calculated from the slopes and intercepts of the plots, respectively (Table 2). The values of the correlation coefficients ($R^2$) for pseudo-

second-order kinetic model obtained were greater than 0.99 for most concentrations. Moreover, the equilibrium adsorption capacity ($q_e$, Cal) derived from Eq. (4.4) also agree well with the experimentally observed data. These results indicated that the adsorption system studied belongs to the " pseudo second-order kinetic model", and lead (II), Cr (III) and Cd (II) ions were adsorbed on the surface of chelating resin via chemical interaction such as ionic or covalent bonds. [52, 53]





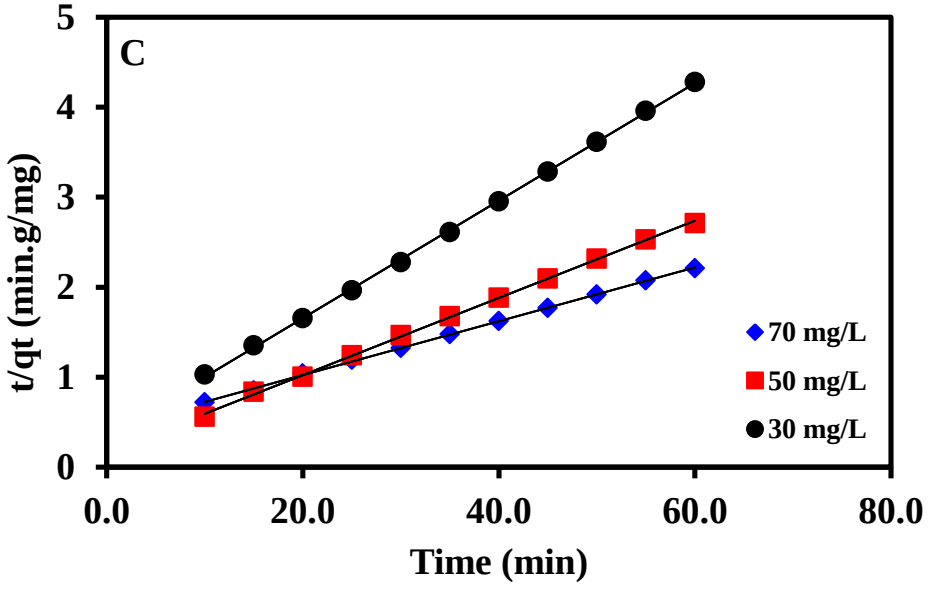



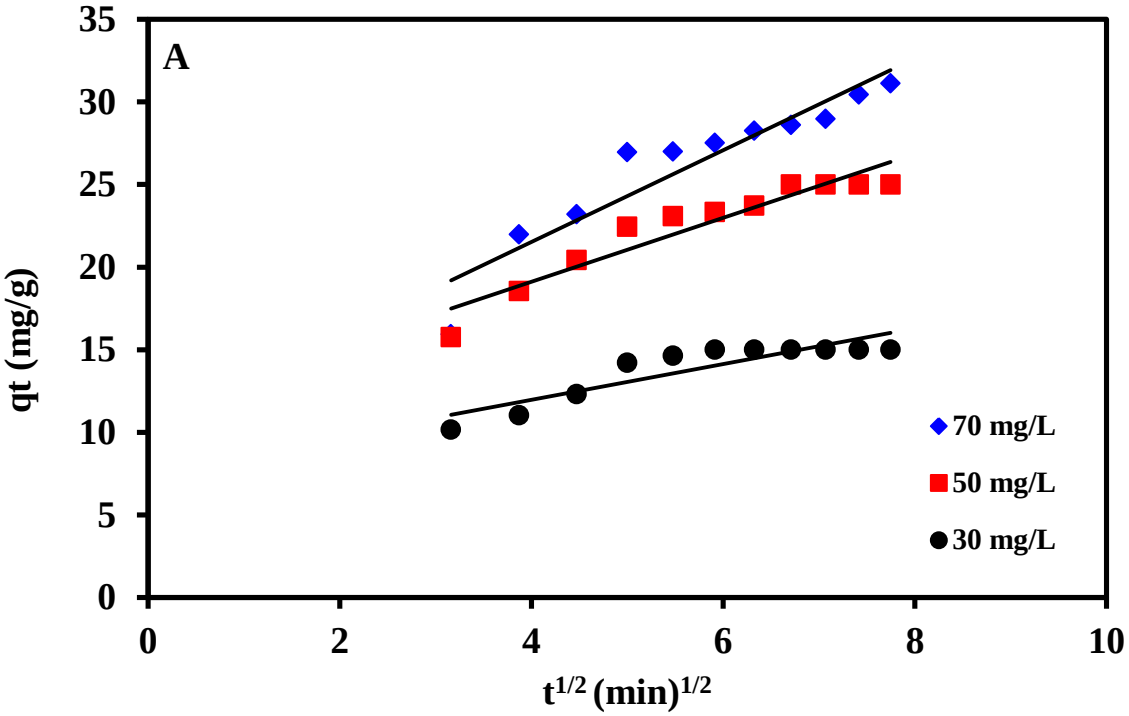

**Figure 15 Pseudo-second-order kinetic plot for adsorption of (A) Pb (II), (B) Cr (III), and (C) Cd (II) on a Chelating resin for different initial feed concentration at pH 5.5 and temperature 25 °C.**

### 4.8.3 The intraparticle diffusion model:

The mechanism of adsorption of lead (II), Cr (III) and Cd (II) onto chelating resin was identified by testing the experimental data of adsorption process onto an intraparticle diffusion model. Many consecutive steps may involve in the sorption of an adsorbate by a porous solid adsorbent, which are (I) the place where the sorbate moved from the bulk solutions to the external surfaces of sorbent and it's called surface diffusion. (II) The movement of the molecules into the interior of sorbent particles and its called intraparticle or pore diffusion. (III) Adsorption on the interior sites of the sorbent. [59] The" intraparticle diffusion model" is expressed as:

$$q_t = k_{id} t^{1l2} + C \qquad (4.8)$$

Where $k_{id}$ is the intraparticle diffusion rate constant (milligrams per gram per $min^{½}$), C is the intercept (milligrams per gram).the plots of $q_t$ versus $t^{1/2}$ are illustrated in Fig. (16) we see that the lines of different concentrations does not go through the point of origin, which means the mechanism cannot determine the rate of the overall process, and adsorption mechanism is seems to be very complex.[53, 56]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t1/2 (min)1/2
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50 mg/L
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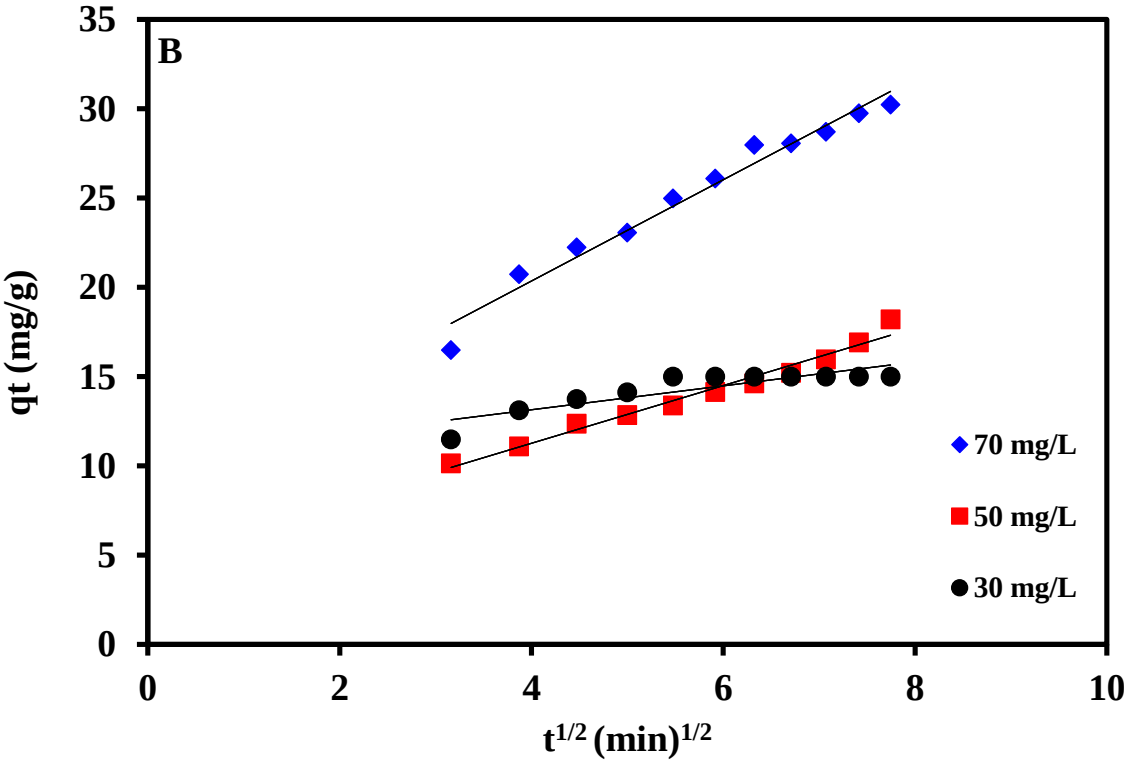
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50 mg/L
30 mg/L

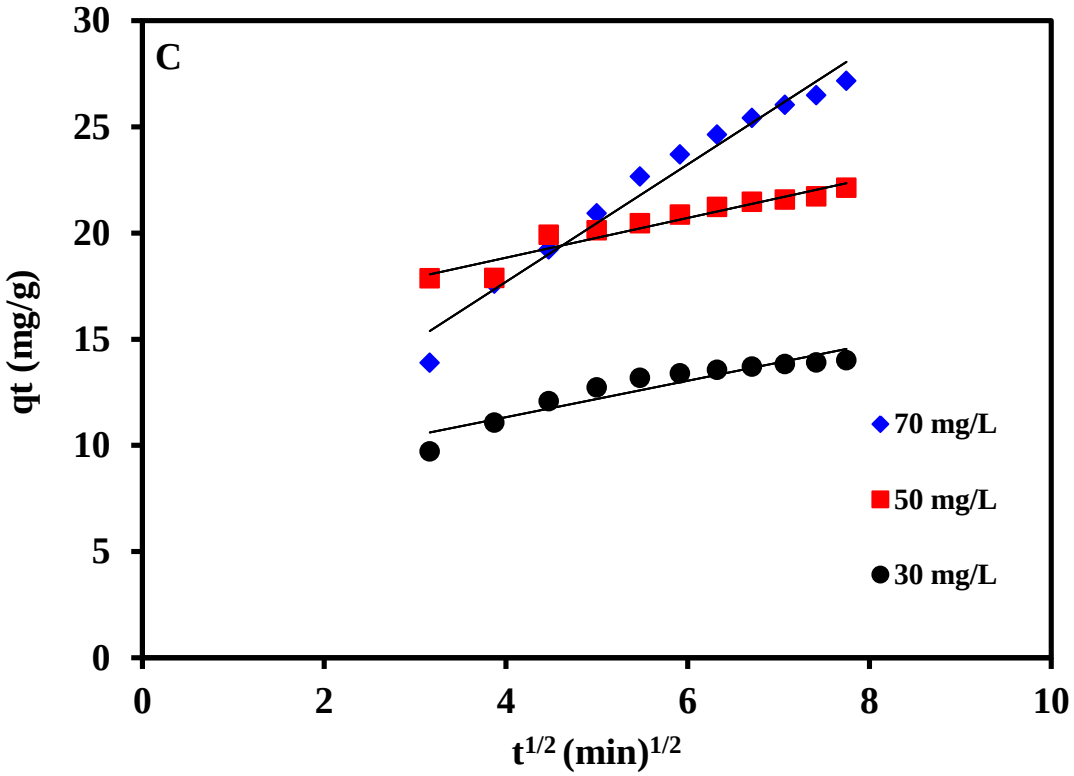



**Figure 16 Intraparticle diffusion kinetic plot for adsorption of (A) Pb (II), (B) Cr (III), and (C) Cd (II) on a Chelating resin for different initial feed concentration at pH 5.5 and temperature 25**

**°C.**

**Table 2 Kinetic constant and parameters obtaind for heavy metal adsorption on hydroxamic resin**

| Metal | | Pseudo-first order | | | | Pseudo-second order | | | | Intraparticle diffusion model | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_i$(mg/L) | $q_e$ exp (mg/g) | $K_1(10^{-3})(min^{-1})$ | $q_e$ cal (mg/g) | $R^2$ | $K_2(^{10-2})$ (g/mg min) | $q_e$ ,cal(mg/g) | *h* (g/min) | $R^2$ | $K_{id}$ (mg/g.min) | C (mg/g) | $R^2$ |
| Pb(II) | 70 | 31.13 | 54.8 | 1303.9 | 0.951 | 0.96 | 36.23 | 2.74 | 0.993 | 2.775 | 10.422 | 0.881 |
| | 50 | 23.72 | 93.3 | 739.3 | 0.620 | 0.45 | 28.65 | 3.70 | 0.998 | 1.935 | 11.374 | 0.897 |
| | 30 | 14.63 | 57.1 | 65.9 | 0.860 | 0.25 | 16.92 | 3.33 | 0.994 | 1.080 | 7.647 | 0.794 |
| Cr(III) | 70 | 30.24 | 53.2 | 1451.4 | 0.966 | 0.22 | 36.23 | 2.86 | 0.997 | 2.834 | 9.023 | 0.972 |
| | 50 | 22.96 | 61.02 | 670.2 | 0.983 | 0.33 | 20.96 | 1.44 | 0.973 | 1.615 | 4.806 | 0.975 |
| | 30 | 14.12 | 51.4 | 53.1 | 0.866 | 2.06 | 15.94 | 5.23 | 0.999 | 0.667 | 10.486 | 0.756 |
| Cd(II) | 70 | 27.16 | 54.1 | 1330.5 | 0.977 | 0.21 | 33.44 | 2.34 | 0.999 | 2.766 | 6.633 | 0.969 |
| | 50 | 22.13 | 61.02 | 191.6 | 0.945 | 1.12 | 23.31 | 6.07 | 0.999 | 0.937 | 15.093 | 0.925 |
| | 30 | 14.02 | 78.50 | 186.6 | 0.995 | 1.20 | 15.34 | 2.80 | 1.000 | 0.858 | 7.903 | 0.881 |

## 4.9 Adsorption isotherm models

Various isotherm models were applied to determine the efficiency of adsorption. In the adsorption of heave metal ions from aqueous solution, and the importance of the adsorption isotherms the description of the fractions of sorbate molecules at equilibrium were splitted between solid and liquid phase. [51,55] "Langmuir and Freundlich adsorption isotherm models" were studied for lead (II), Cr (III) and Cd (II) adsorption on chelating resin.

### 4.9.1 The Langmuir isotherm model

The "Langmuir model" presumes that the surface was homogenous with a finite number of adsorption sites in the process of uptake of adsorbate molecules, also suggested that the kind of adsorption is monolayer adsorption. Once site is filled by adsorbate molecule that means surface is reach the saturation point and no chance for more adsorption in this site. [52, 60, 74] The linear equation can express as:

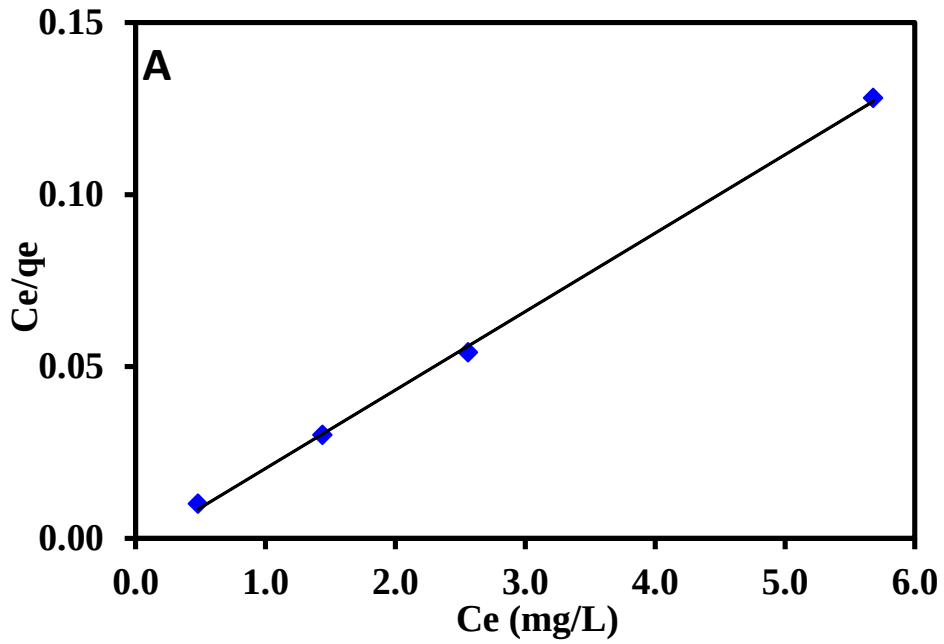
$$\frac{C_e}{q_e} = \frac{1}{k_l q_m} + \frac{C_e}{q_m} \qquad (4.9)$$

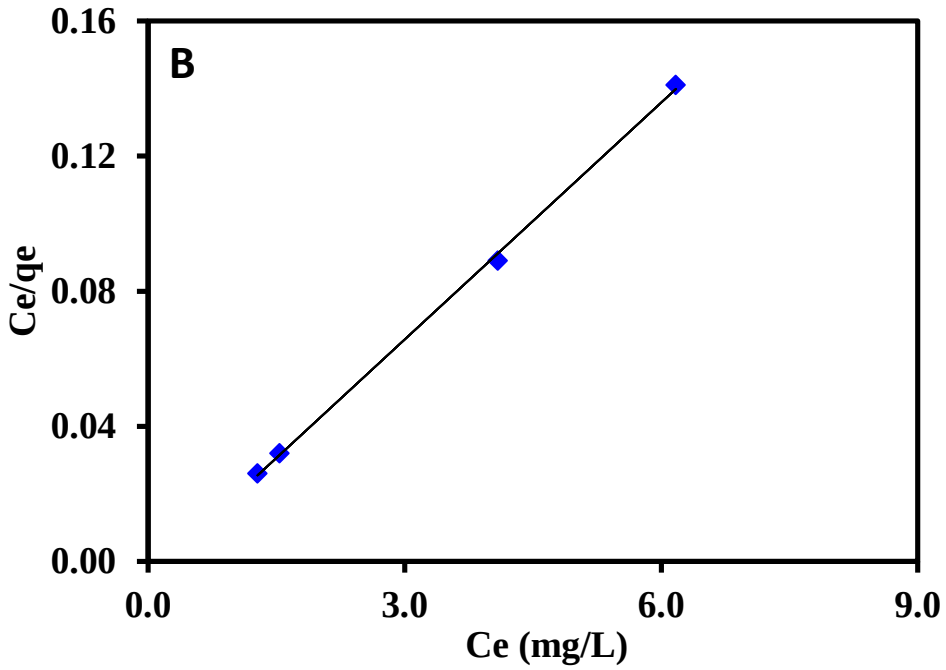
Where $q_e$ is the amount of metal ions adsorbed (mg/g) at equilibrium $C_e$ is the equilibrium concentration (mg/L) of metals in solution, $q_m$ gives the maximum theoretical monolayer adsorption capacity (mg/g) and $K_L$ is Langmuir equilibrium constant (L/mg) and it's related to the affinity of adsorption sites. From the plot of $C_e/ q_e$ versus $C_e$ can obtain the values of $q_m$ and $K_L$ from the slope and intercept respectively, also correlation coefficients ($R^2$) Table. (3), moreover from the linearity of the plot we can indicate that the Langmuir adsorption isotherm is applicable Fig (17) as the result of that we assume the formation of monolayer on the surface of adsorbate. [61] The experimental data showed high correlation with Langmuir model. Separation factor ($R_L$) is the characteristic

dimensionless equilibrium parameter for this model, defined by Weber and Chakkravorti [62]:

$$R_L = \frac{1}{1+K_L C_o} \qquad (4.10)$$

Where $K_L$ (L/mg) is the Langmuir constant and $C_o$ (mg/L) is the lowest initial concentration of metal ions from the average value of ($R_L$) for each initial concentration in Table. (4.2) we find its less than unity and greater than zero which mean the favourable adsorption of lead (II), Cr (III) and Cd (II) on hydroxamic chelating resin,[63] which indicate that the isotherm data fit this model well.





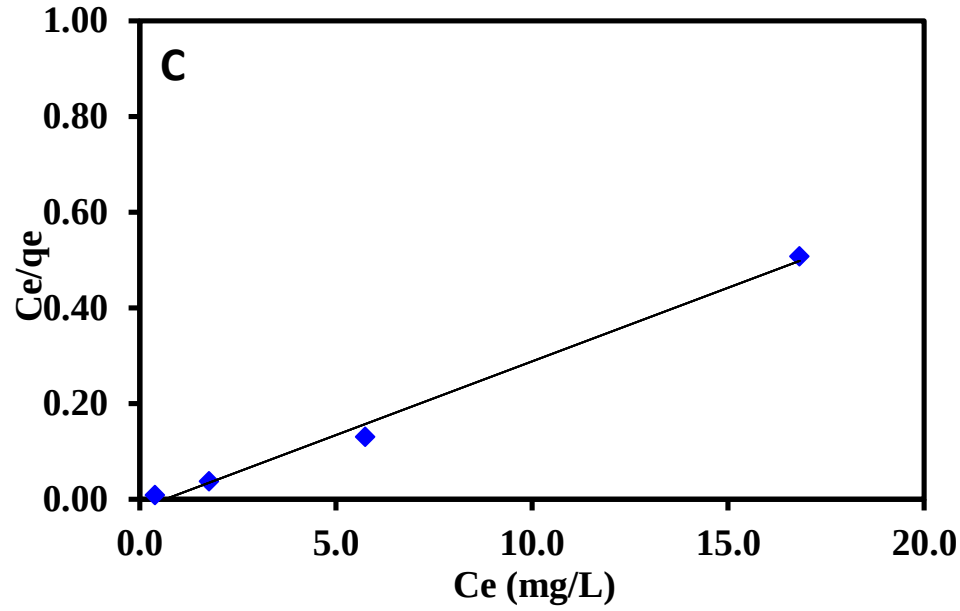



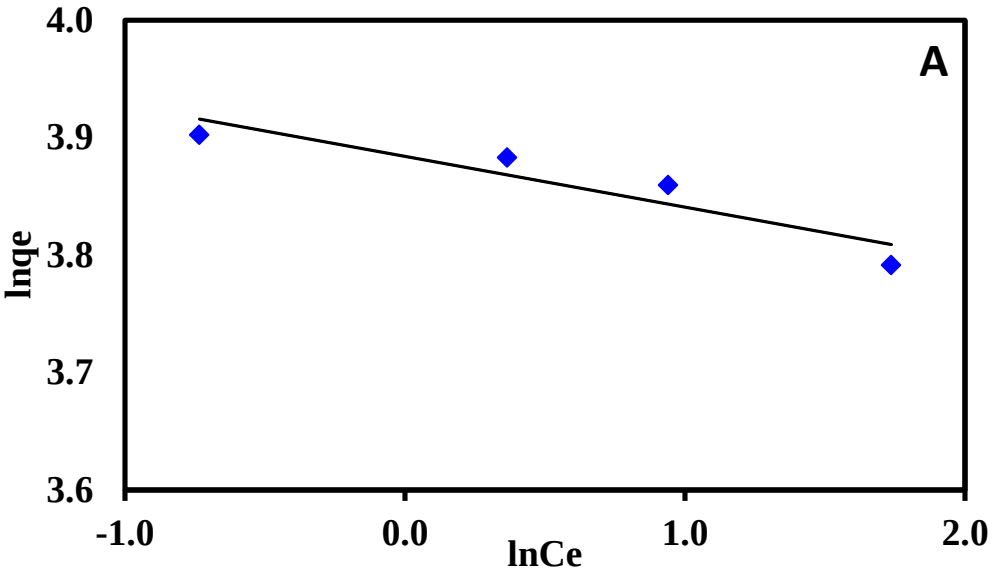

**Figure 17 Langmuir adsorption isotherms for adsorption of (A) Pb (II), (B) Cr (III), and (C) Cd (II) on a chelating resin, pH 5.5 and temperature 25 °C.**

### 4.9.2 Freundlich isotherm model

The Freundlich model usually used to investigate if the adsorbate molecule adsorbed onto solid adsorbent with heterogeneous surface. [51, 75] The mass of chelating resin was fixed and various initial concentrations of lead (II), Cr (III) and Cd (II) were applied to obtain the equilibrium data. The linear equation of "Freundlich isotherm model "defined as:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \qquad (4.11)$$

Where $K_f$ (mg/g) is adsorption capacity and 1/n (g/L) is adsorption intensity which are Freundlich adsorption constants. $Lnq_e$ against $lnC_e$ was plotted and straight lines were obtained for adsorption of lead (II), Cr (III) and Cd (II) in chelating resin Fig. (18). The values of Freundlich adsorption constants $K_f$ and n were determined from the intercepts and slopes of the same plot and listed in Table.(3), the values of correlation coefficient ($R^2$) give an indication of a poor agreement between experimental data and Freundlich model. Also the value of n was more than unity that means favourable adsorption conditions and metal ions are favourably adsorbed by the prepared chelating resin. [64]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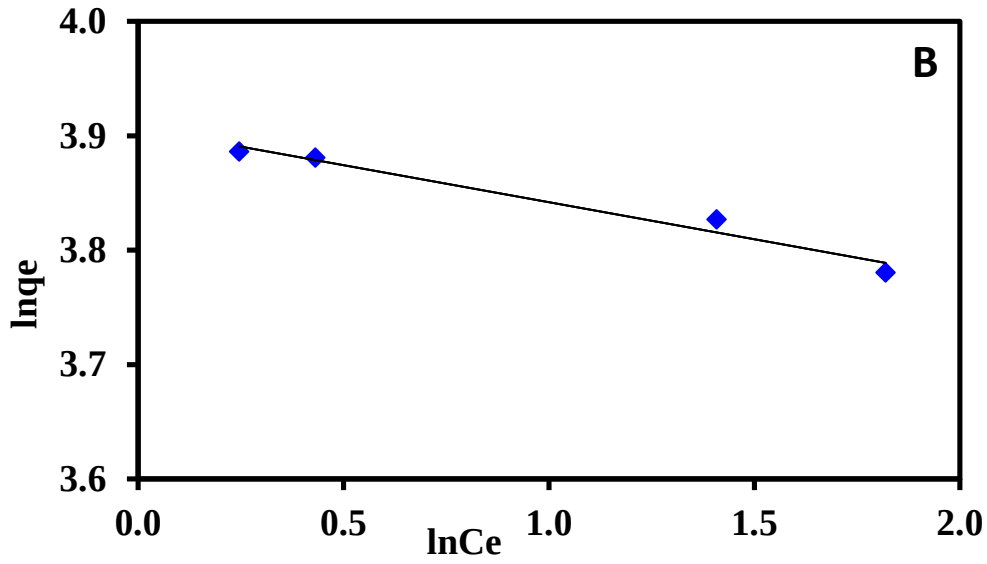
3.8
3.7
3.6
lnqe
-1.0
0.0
1.0
2.0
lnCe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lnqe
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0.5
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lnCe

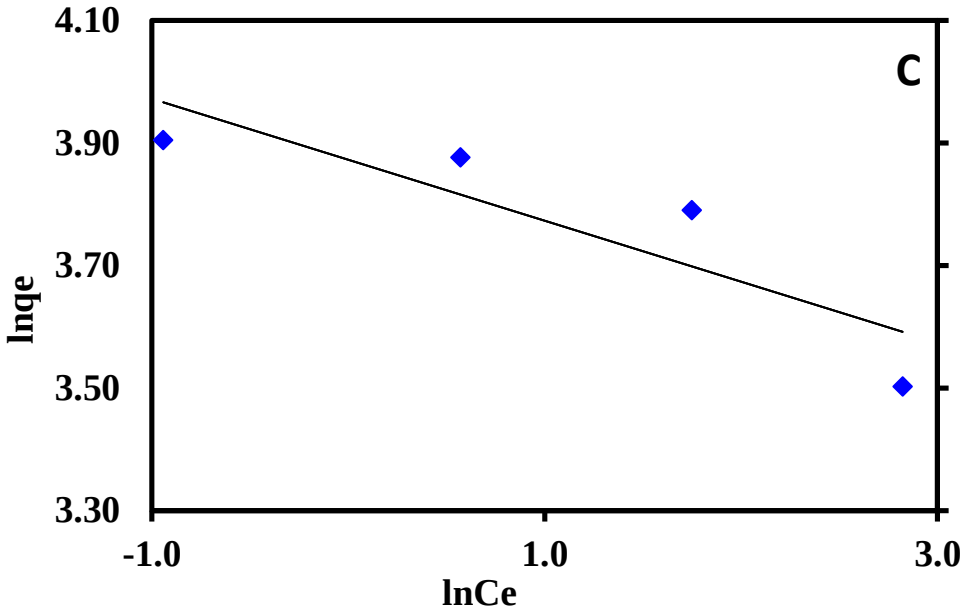



**Figure 18 Freundlich adsorption isotherms for adsorption of (A) Pb (II), (B) Cr (III), and (C) Cd (II) on a chelating resin, pH 5.5 and temperature 25 °C.**

**Table 3 Langmuir and Freundlich isotherm constants for Lead (II), Cr (III) and Cd (II) adsorption on Chelating resin**

| Metal | T (k) | Langmuir isotherm constants | | | | Freundlich isotherm constants | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $q_m$ (mg/g) | $K_L$ (L/mg) | $R_L$ | $R^2$ | 1/n | n | $K_F$ | $R^2$ |
| Pb(II) | 298.16 | 43.86 | 9.12 | 0.002 | 0.999 | 0.04 | 23.15 | 48.62 | 0.8638 |
| Cr(III) | 298.16 | 42.74 | 5.32 | 0.004 | 0.999 | 0.06 | 15.43 | 49.74 | 0.9701 |
| Cd(II) | 298.16 | 32.47 | 1.54 | 0.012 | 0.9932 | 0.10 | 10.04 | 48.07 | 0.7647 |

# CHAPTER 5

# Removal using Poly-(amidoxime) Resin

## 5.1 Graft copolymerization

DPWF was treated with mixed solution of (hydrogen peroxide and ferrous ammonium sulfate) to initiate a free radicals in the backbone of fiber and provide cellulose macro-radical. Graft copolymerization took place after adding Acrylonitrile (AN) monomer to the mix, the cellulose macro-radical attacked the double bond in AN and a covalent bond between monomer and cellulose appeared, the chain initiated with continues creation of free radical on the AN. chain propagates grafting onto the cellulose was possible by adding AN monomer subsequently. At the end the reaction terminate either by forming copolymer by reaction of two macro-radical or formation of homopolymer by reaction of two monomer radicals. Fig (19) explain the whole process. [40, 65]

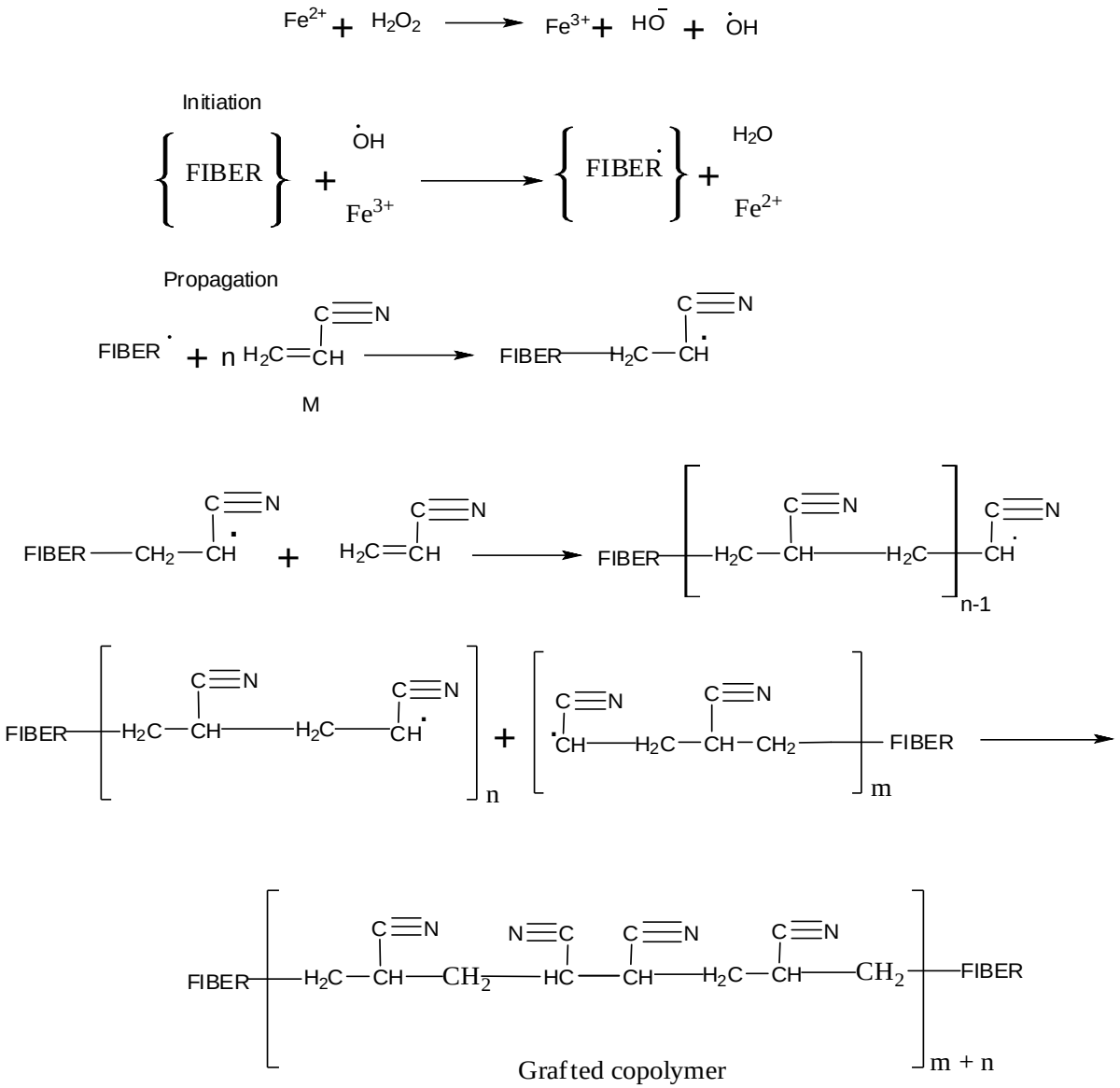



**Figure 19 Mechanism of graft copolymerization of Acrylonitrile onto DPWF**.

## 5.2 Optimization of grafted polymerization parameters

Various parameters effect on the yield of grafted copolymerization such as temperature, time of reaction, monomer volume, cocatalyst amount and concentration of initiator, all these parameters were studied separately to investigate the best conditions and obtain the best yield.

### 5.2.1 Effect of temperature

A wide rang of temperatures was applied to obtain the best yield of grafted copolymer. Fig. (20) illustrate the effect of temperature, we can see clearly the increasing of % yield of grafting with increasing the temperature from 30 ºC up to 75 ºC, and this increasing can refer to increasing of diffusion of the monomer to reach the active sites on the backbone of substrate with increasing of temperature. But when temperature rise more than 75 ºC the monomer will start to evaporate and hydrogen peroxide will decompose this lead to creation of huge number of free radicals, the yield of homopolymer will increase and % of grafted copolymer will decrease.[48, 66]

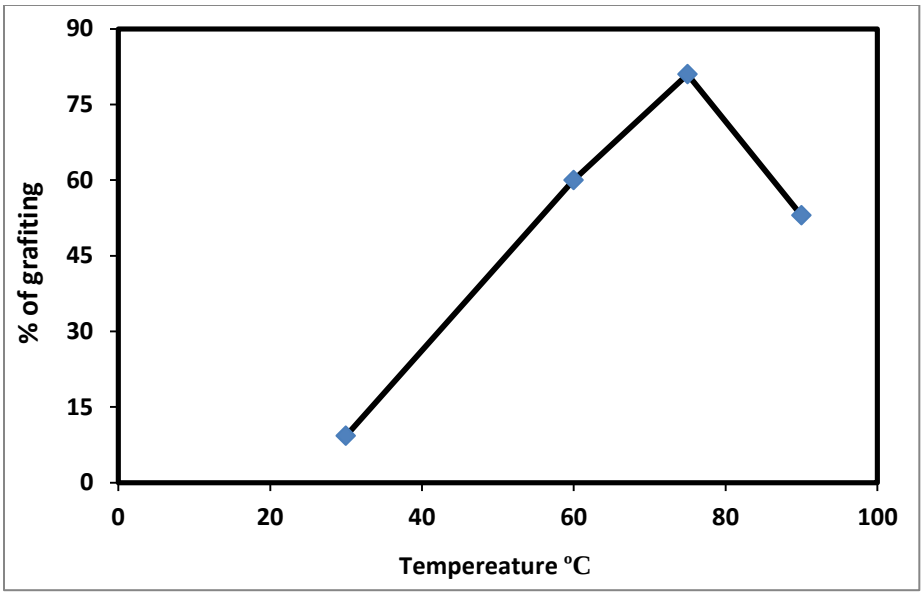



**Figure 20 Effect of reaction temperature on the % of grafting. Reaction time 60 min, AN 8 ml, $H_2O_2$ 0.03 M, $Fe^{+2}$ 0.3 mmol.**

### 5.2.2 Effect of the concentration of initiator

The concentration of initiator affect clearly on yield of grafted copolymer, as shown in Fig. (21) the % of grafting raised with increasing of concentration of the hydrogen peroxide that due to increasing the production of free radicals in active sites of the fiber, the percentage of grafting reach 81% with 0.03 M of hydrogen peroxide, this percentage decrease with increasing this concentration, because the termination step will take place by reaction of cellulosic radicals together before adding the monomer, moreover in higher concentrations the yield of homopolymer increase. [3]

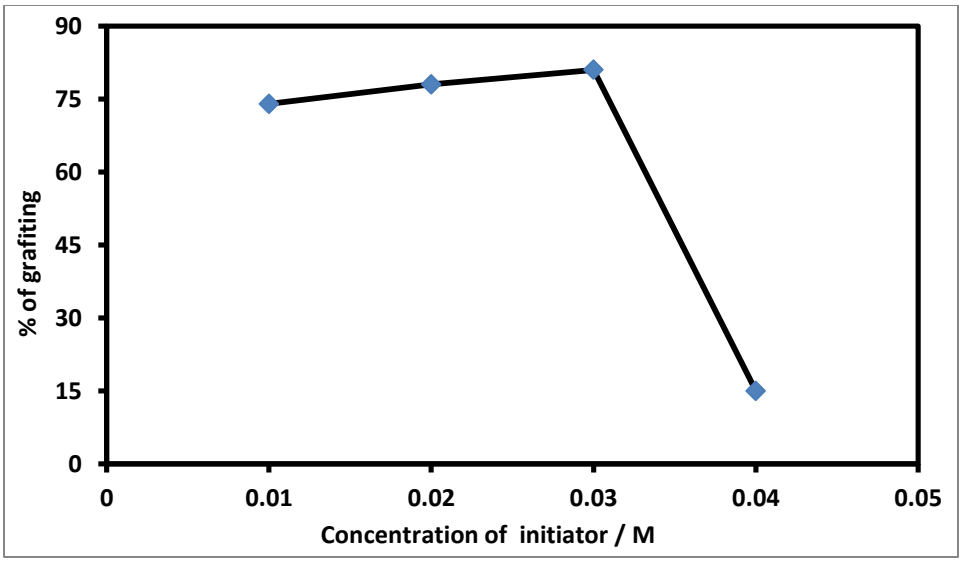



**Figure 21 Effect of the amount of initiator $H_2O_2$ on the % of grafting. Reaction time 60 min , AN 8 ml, Temperature 75 °C, $Fe^{+2}$ 0.3 mmol.**

### 5.2.3 Effect of the amount of monomer

The percentage of grafting rise with increasing of the volume of the (AN) monomer this can be attributed to the availability of huge number of monomer molecules reach the active sites in the backbone of fiber, but on the other hand from Fig. (22) we can see clear decreasing in the percentage of grafting with increasing of the volume over 8ml because the possibility of homopolymerization increase. [48]

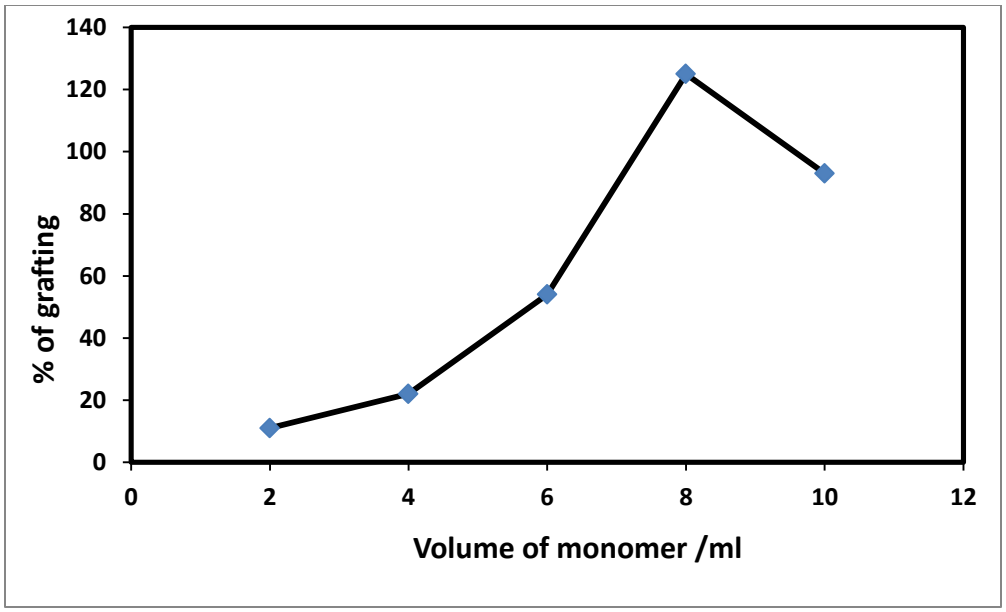



**Figure 22 Effect of the amount of monomer (AN) on the % of grafting. Reaction time 60 min, $H_2O_2$ 0.03 M, Temperature 75 °C, $Fe^{+2}$ 0.3 mmol.**

### 5.2.4 Effect of reaction period

The reaction time play significant role in the yield of grafting, with increasing the time all monomer molecules can reach all active sites on the backbone until 60 min its gave the best yield of grafting, after that all active sites were covered and concentration of all reaction species became less this lead to low yield of grafting and almost remaining constant with increasing time, [67] this explanation agree with Fig. (23).

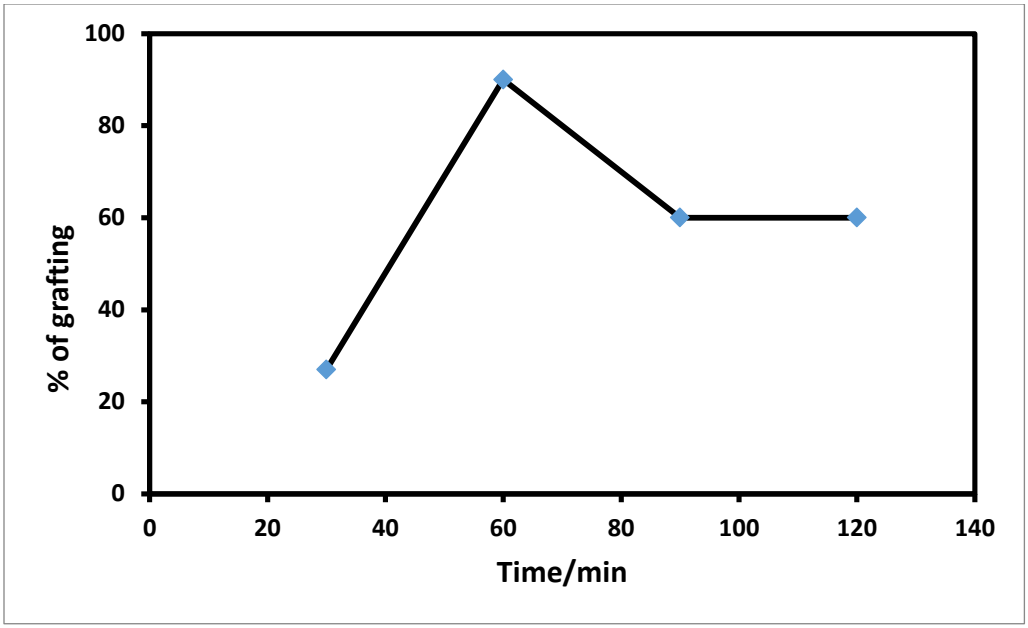



**Figure 23 Effect of reaction period on the % of grafting and efficiency. AN 8 ml, $H_2O_2$ 0.03 M, Temperature 75 °C, $Fe^{+2}$ 0.3 mmol.**

### 5.2.5 Effect of the amount of catalyst

Small amount of ammonium ferrous sulphate [$(NH_4)_2SO_4.FeSO_4.6H_2O$] witch is catalyst of grafting reaction was enough for the best yield of product as we see in Fig. (24), 0.306 mmol from catalyst gave 81% of grafting product, this yield decrease with increasing of this amount of catalyst we can attributed that to presence of huge number of radicals due to hydrogen peroxide decomposition enhancement by the catalyst this lead to termination of reaction by reaction of radicals together and yield will decrease. [45, 68]

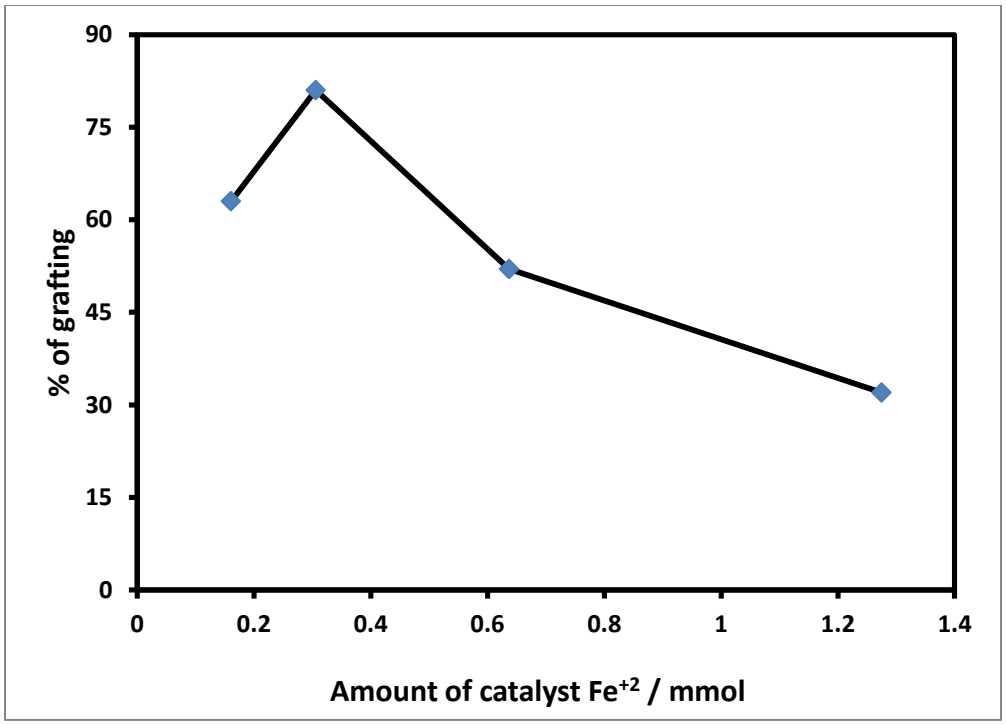



**Figure 24 Effect of the amount of catalyst $Fe^{+2}$on the % of grafting.AN 8 ml, $H_2O_2$ 0.03 M, Temperature 75 °C, 60 min**

## 5.3 Preparation of poly-(amidoxime) resin

The AN-DPWF grafted copolymer that contain nitrile group was treated by hydroxylamine hydrochloride at pH=11 to convert the nitrile to amidoxime. This reaction was done for 3 hours, temperature 75°C and the ratio between grafted copolymer and hydroxylamine 1:1 in methanolic solution, the mechanism of this conversion showed in Fig. (25).

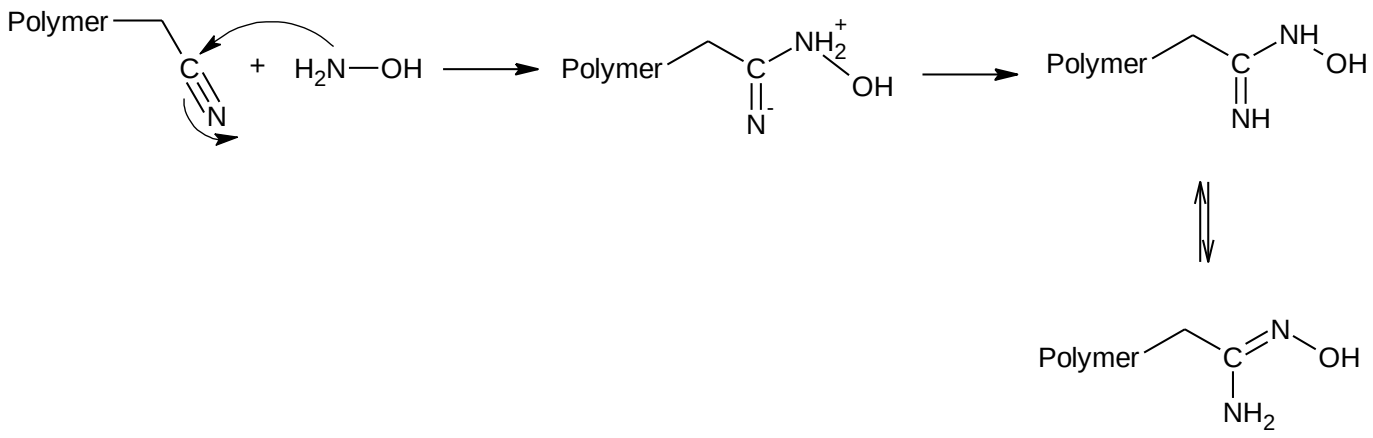



**Figure 25 Reaction mechanism of preparation of poly amidoxime resin.**

## 5.4 Characterization of AN-DPWF grafted copolymer and resin

FT-IR spectra was obtained for DPWF, grafted copolymer and amidoxime resin to confirm the completion of polymerization and conversion to chelating resin. From Fig. (26) we can see the same characteristic adsorption bands for DPWF such as broad adsorption band between 3000–3500 cm-$^{-1}$ assigned to O-H stretching vibration and bands appeared at 2900 and 1020 cm$^{-1}$ for C-H stretching and bending modes, respectively. Avery characteristic adsorption at 2240 cm$^{-1}$ for C≡N stretching modes to confirm the presence of acrylonitrile onto the backbone of DPWF and grafting reaction complete. [40] This band was disappeared completely after conversion to amidoxime resin and new adsorption band formed at 1650 cm$^{-1}$ associated to C=N vibration of amidoxime group. Another adsorption band observed at 941 cm$^{-1}$ may be assigned to the N–O bond of the oxime group. [69] Scanning electron microscope (SEM) images were taken for DPWF before and after polymerization to investigate the changes on morphology of the fiber surface, Figs. (27) and (28) showed the surface of the fiber before and after grafted polymerization, respectively. All pours on the DPWF surface were covered by poly

acrylonitrile (PAN) via chemical bond and provide homogeneous surface with less porosity.

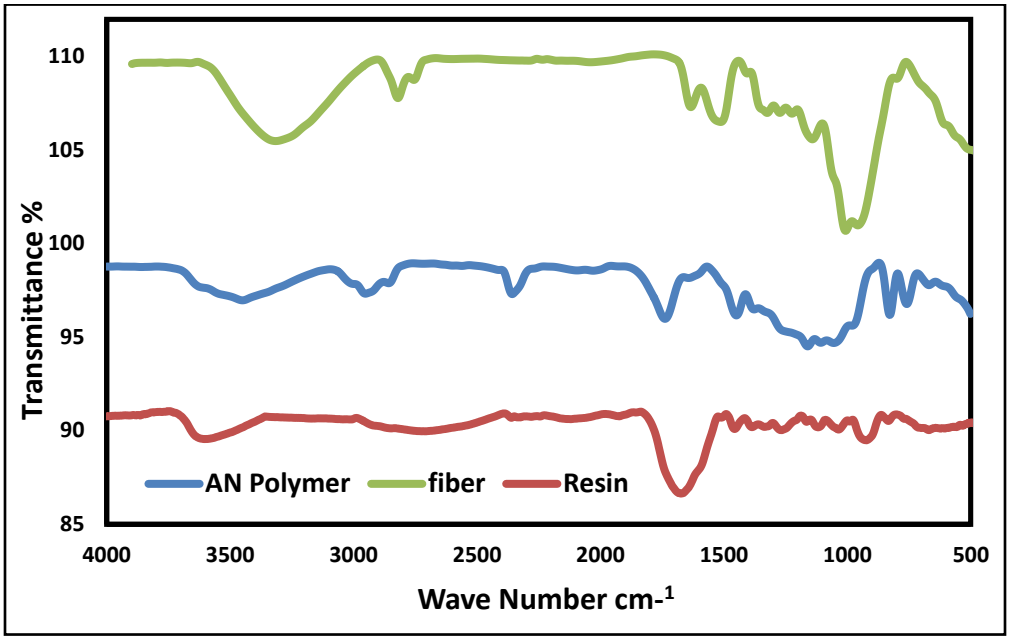



**Figure 26 FTIR DPWF fiber (top- gray), PAN-g-DPWF fiber (middle - blue) and resin containing amidoxime groups (Bottom – orange)**

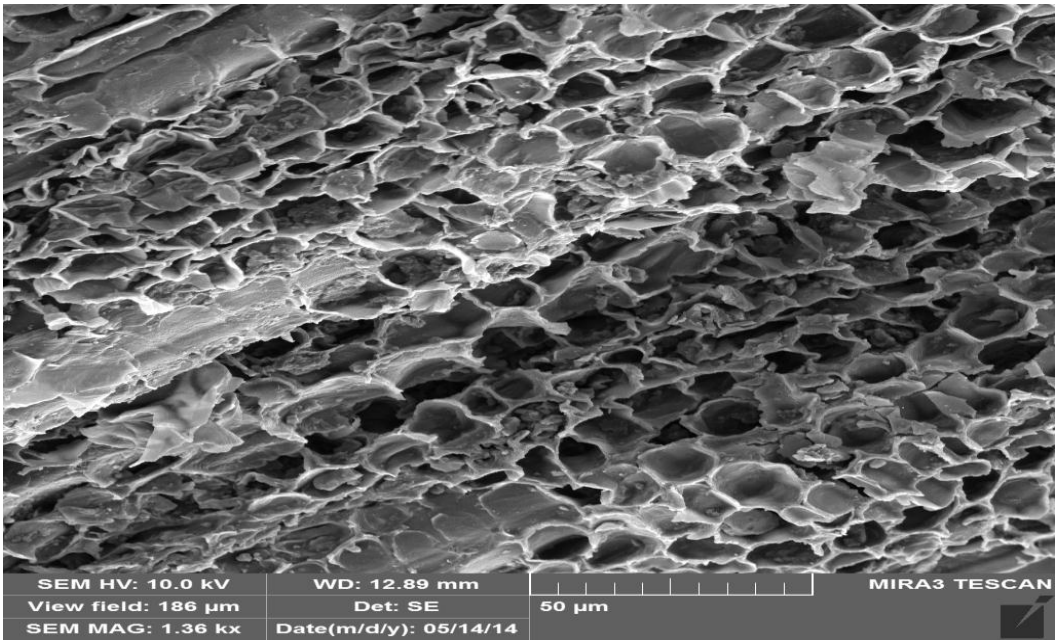



**Figure 27 Scanning electron micrographs of DPWF before grafting, SEM MAG. (1.36 KX)**

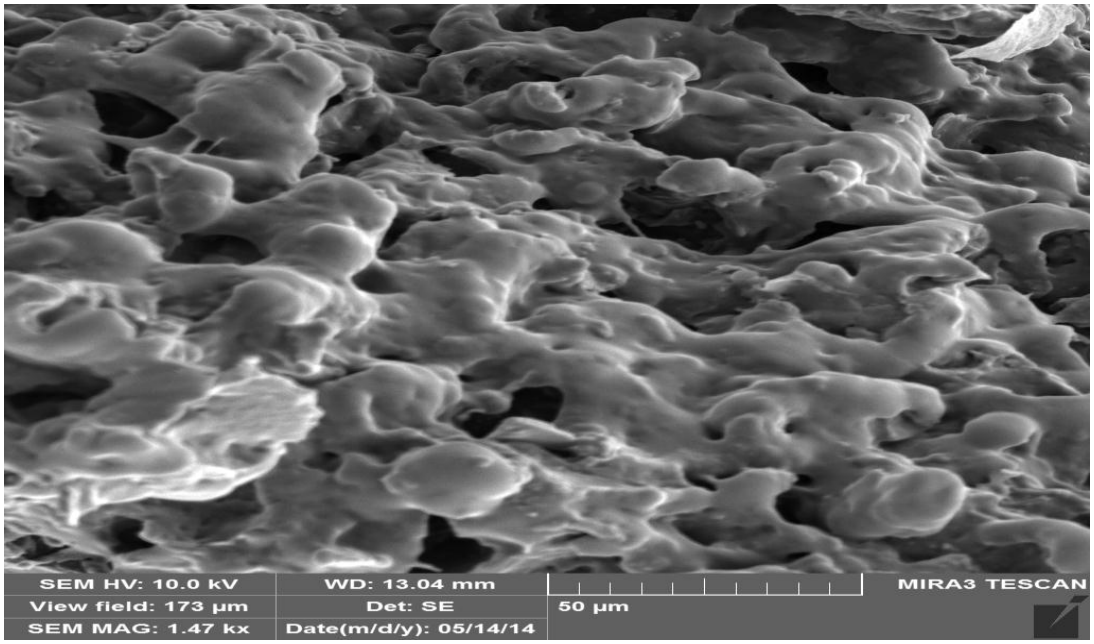



**Figure 28 Scanning electron micrographs of DPWF after grafting, SEM MAG. (1.47 KX)**

## 5.5 Effect of initial pH

Batch technique was conducted to investigate the optimum pH for removal heavy metals using amidoxime chelating resin. The concentration of the counter ions on the resin, ability of ionization and solubility of adsorbates all these depend on pH. [51] wide range from 1.0 to 6.0 was used to get the optimum pH with constant concentration of metals and same dosage of resin at 25 °C. The adsorption of lead (II), Cr (III) and Cd (II) was maximum in the pH=5.0 as we see in Fig. (29).

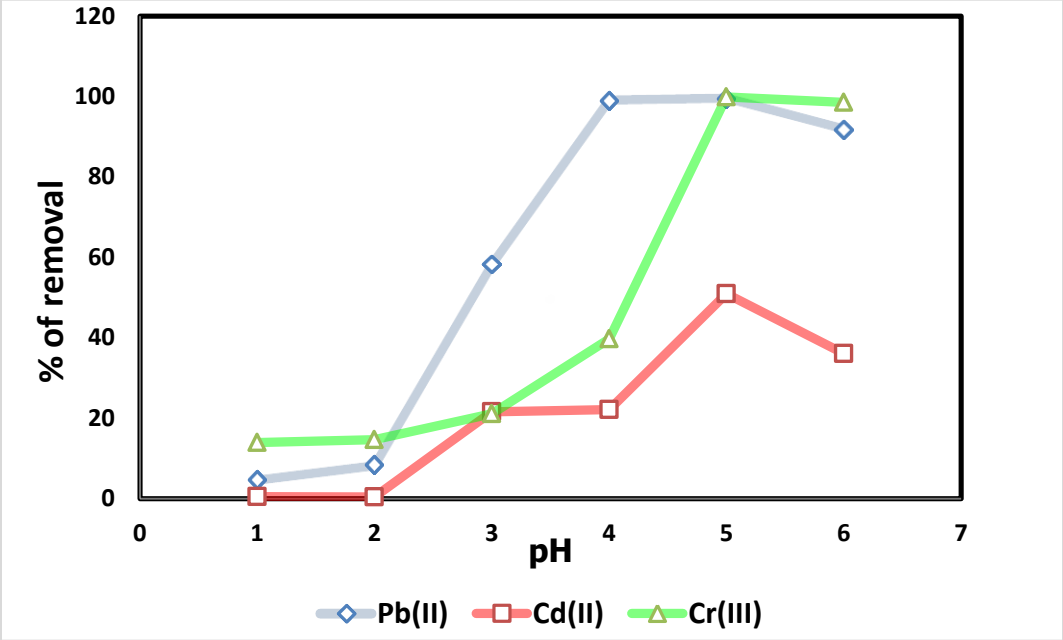
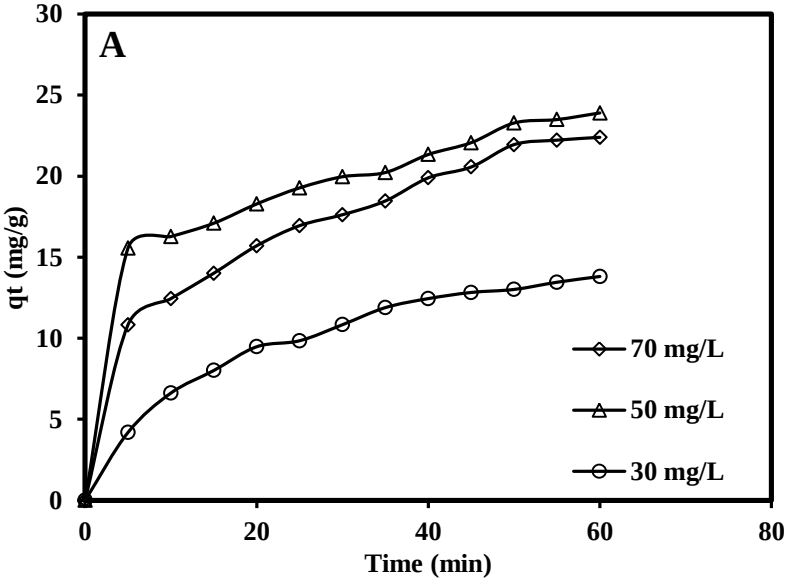


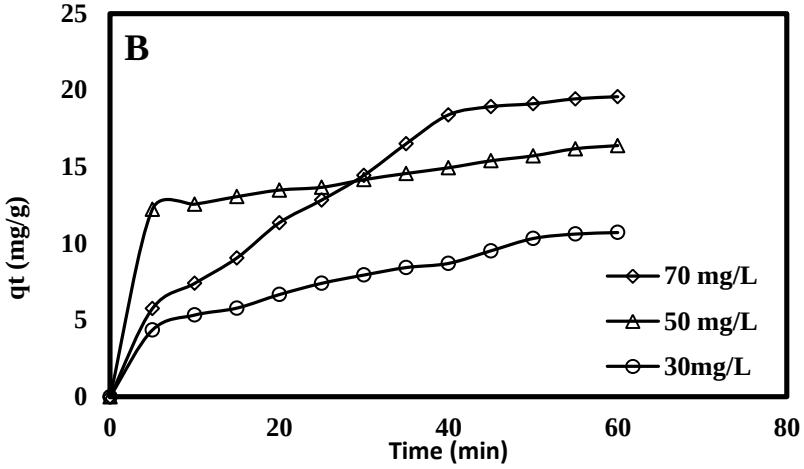

**Figure 29 Effect of pH on the adsorption of ($Pb^{+2}$) ($Cr^{+3}$) and ($Cd^{+2}$) ions, dosage of chelating resin 1g ions concentration 50 mg/L, time 60 min, and temperature 25 °C.**

## 5.6 Effect of contact time and initial concentration

The contact time is one of important parameter to study, its affect clearly in adsorption of heavy metals onto chelating resin, from Fig. (30) we can see that the adsorption of heavy metals increase with increasing of the contact time, also the adsorption is fast in the

beginning until reach equilibrium at 35 min after that the value of qt (mg/g) remain constant, this can be attributed to the availability of active sites on the surface of chelating resin in the beginning of reaction. [55] Initial concentration of metals under study lead (II), Cr (III) and Cd (II) was effect on removal of these metals, increasing of metal ion initial concentration increase the amount of metal ions adsorbed qt (mg/g). This can illustrate by ratio of available surface to initial metal ion concentration, on higher concentration this ratio was low and it increase in the lower concentration, then the initial concentration effect on removal of heavy metals. [70]





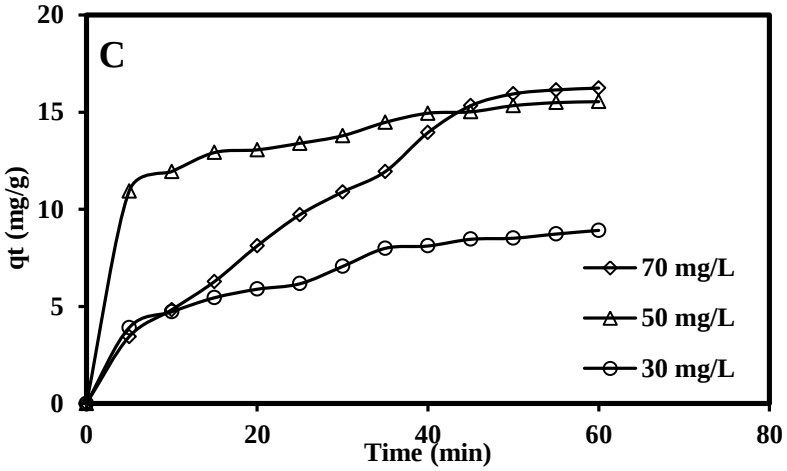




**Figure 30 Effect of contact time on (A) lead (II), (B) Cr (III) and (C) Cd (II) adsorption at different initial feed concentration, solution pH 5, and temperature 25 °C.**

## 5.7 Effect of adsorbent dosage

The amidoxime chelating resin dosage was been investigated for given initial concentration to determine the efficiency of resin, adsorption of lead (II), Cr (III) and Cd (II) was studied with different dosage of resin and 50 mg/L as initial concentration of metals at 25 °C and pH=5. As we see in Fig. (31) the percentage of removal from 61.1% to 87.84% for Lead (II), from 49.94 to 71.50 % for chromium (III) and from 50.26 to

67.48 for cadmium (II) when the resin dosage increase from 0.05 g/L to 0.2g/L, the huge surface area and number of active sites provided by high dosage of resin to constant concentration of metal ions solution could be a good explanation for increasing of percentage of removal. Eq. (5.1) used to calculate the percentage of removal using this resin. [52, 54, 71]

$$\% \text{ of Removal} = \frac{C_o - C_e}{C_o} \times 100 \qquad (5.1)$$

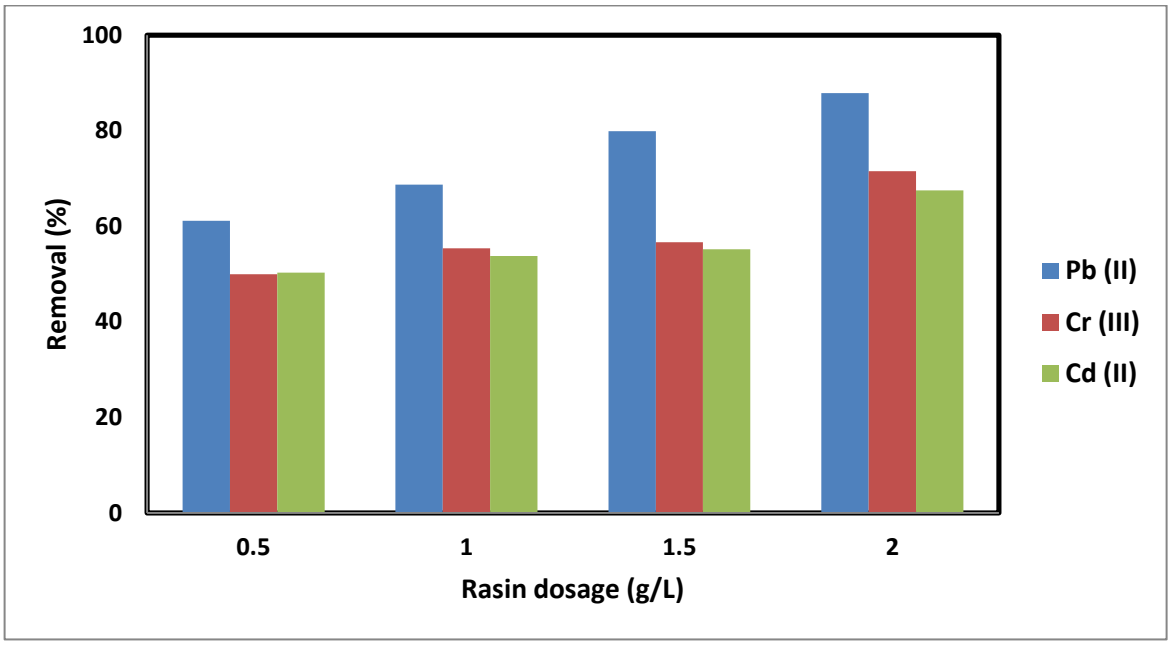



**Figure 31 Effect of adsorbent dosage on adsorption of lead (II), Cr (III) and Cd (II), initial concentrations 50 mg/L, time 60 min, solution pH 5, and temperature 25 °C.**

## 5.8 Adsorption kinetics

To investigate the adsorption mechanism and reaction pathways some adsorption kinetic studies were conducted, various kinetic models were applied to analyse the adsorption process of lead (II), Cr (III) and Cd (II) onto chelating resin such as "pseudo first- order,

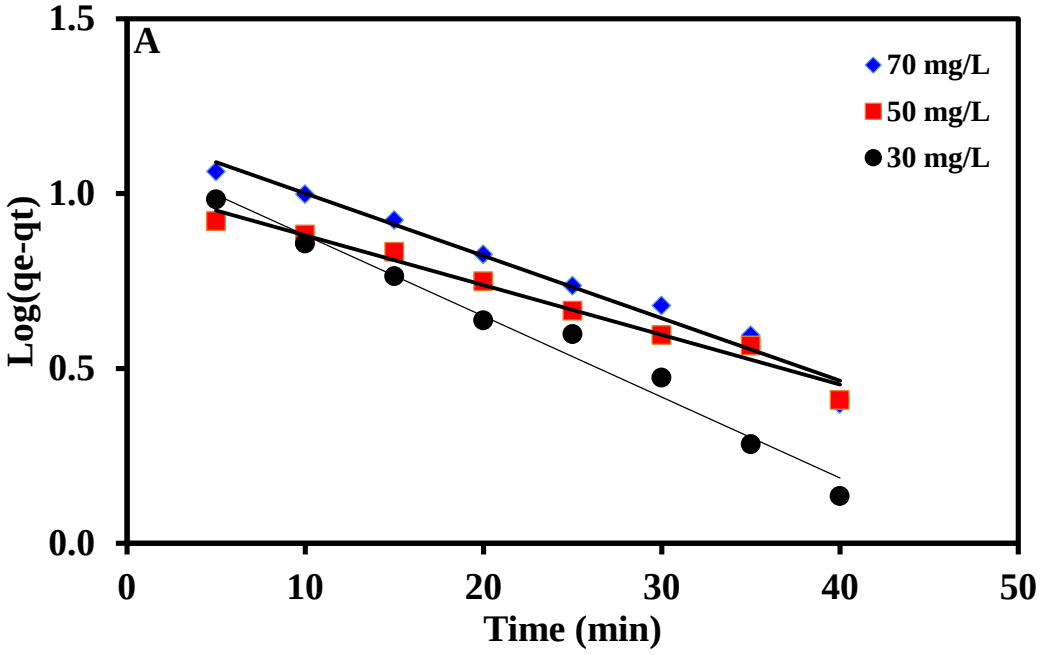
pseudo-second-order and intraparticle diffusion". Models with high correlation coefficients ($R^2$) may describe the adsorption of metal onto chelating resin.

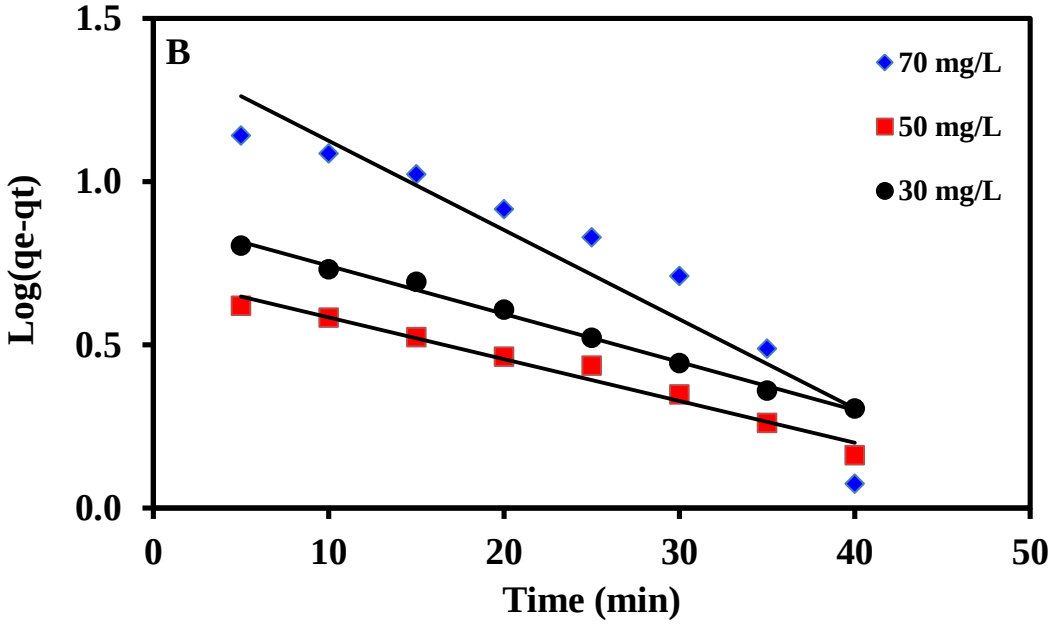
### 5.8.1 The pseudo-first-order model

The "pseudo-first-order kinetic model", illustrate the adsorption mechanisms in solid–liquid systems, is generally expressed as:

$$\mathrm{Log}(q_e - q_t) = \mathrm{Log}\, q_e - \frac{k_1\, t}{2.303} \qquad (5.2)$$

Where $k_1$ is the rate constant of "pseudo-first-order "adsorption (per minute) and qt and $q_e$ are the quantity of metal ions adsorbed (milligrams per gram) at time t, and at equilibrium, respectively. [56, 71] The plots of log ($q_e$ – $q_t$) versus t demonstrated in Fig. (32), give the value rate constant $k_1$ and adsorption density $q_e$ from the slope and intercept respectively (Table 4), bad linearity was obtained for this model this was clear from the values of correlation coefficients ($R^2$) it was low for different concentrations. Moreover there was no any agreement between the experimentally observed equilibrium adsorption ($q_e$, exp) and that derived theoretically ($q_e$, cal), that means the adsorption of metal ions onto chelating resin kinetic data were not fitted with the "pseudo-first-order kinetic model".


A
70 mg/L
50 mg/L
30 mg/L
Log(qe-qt)
Time (min)
1.5
1.0
0.5
0.0
0
10
20
30
40
50


B
70 mg/L
50 mg/L
30 mg/L
Log(qe-qt)
Time (min)
1.5
1.0
0.5
0.0
0
10
20
30
40
50

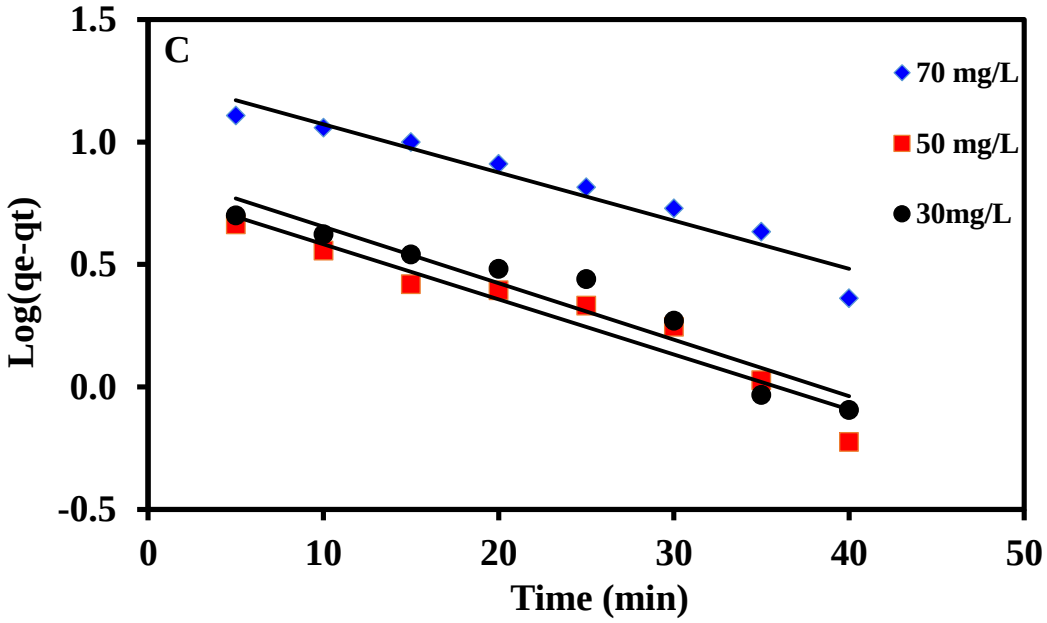



**Figure 32 Lagergren first-order plot for adsorption of (A) Pb (II), (B) Cr (III), and (C) Cd (II) on amidoxime chelating resin for different initial feed concentration at pH 5 and temperature 25 °C.**

### 5.8.2 The pseudo-second-order equation

The "pseudo-second-order adsorption kinetic" rate expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5.3)$$

Where $k_2$ is the rate constant of the "pseudo-second-order" sorption (g/mg.min), $q_e$ and $q_t$ are the sorption capacity at equilibrium and time t (mg/g), respectively. For the boundary conditions t = 0 to t = t and $q_t$ = 0 to $q_t$ = $q_t$, the integrated form of Eq. (5.3) will be as:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (5.4)$$

Equation (5.4) can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e^2}} + \frac{t}{q_e} \quad (5.5)$$

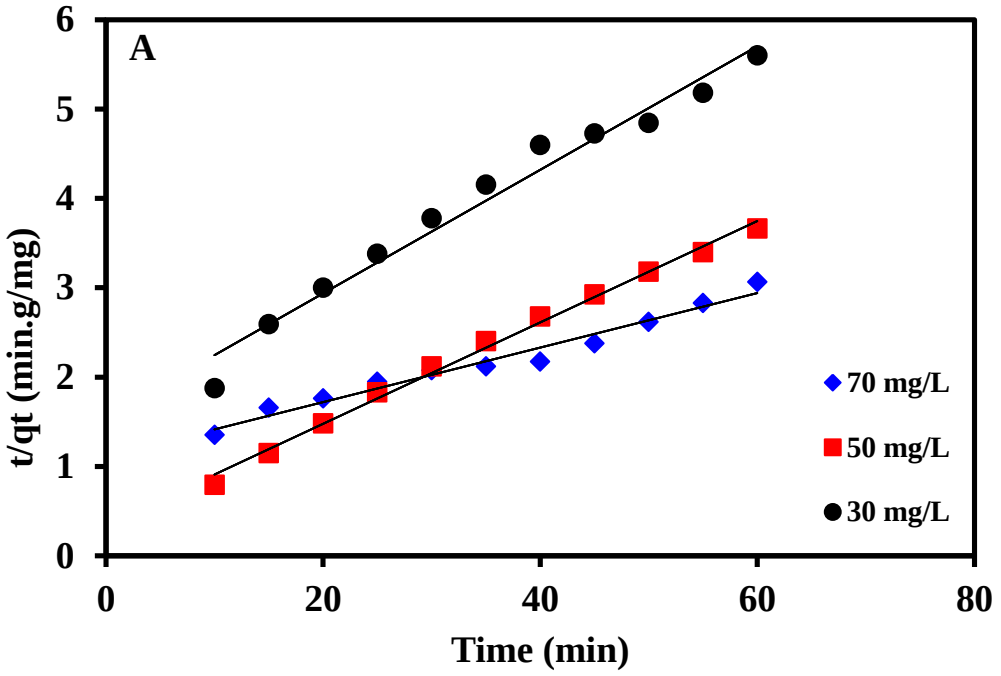
The initial adsorption rate, h (milligrams per gram per minute) is given as:

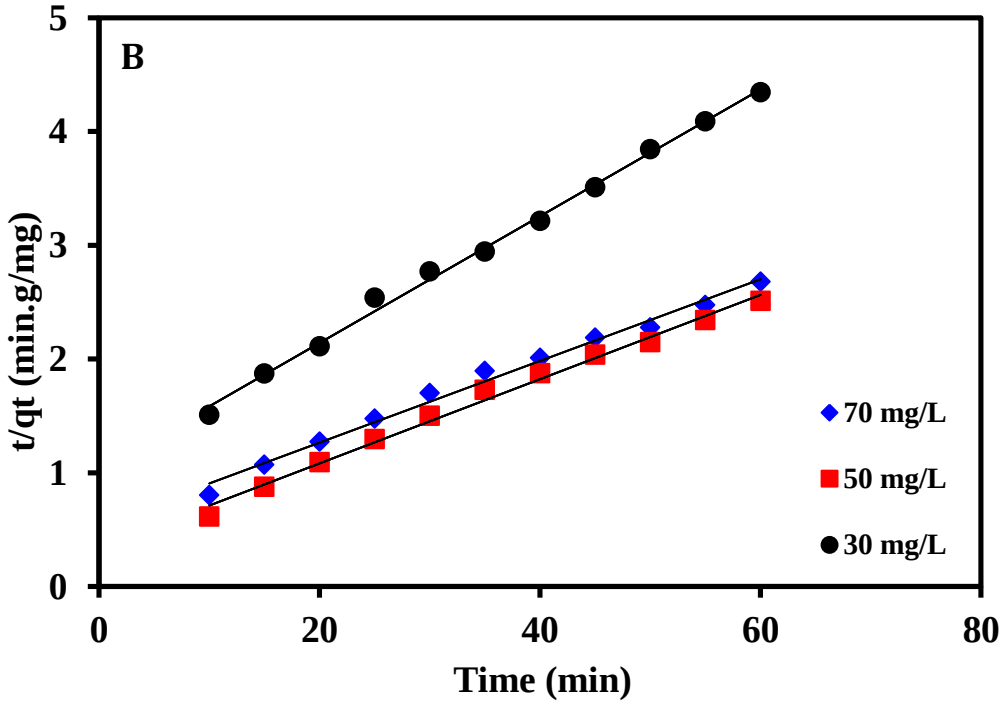
$$h = k_2 \; q_{e^2} \quad (5.6)$$

Eq. 5.5 also can be written as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (5.7)$$

The plots of $t/q_t$ versus t from Eq. (5.7) at different concentrations of lead (II), Cr (III) and Cd (II) showed in Fig. (33). from slope and intercept we calculated the adsorption parameters $q_e$ (Cal.) and $k_2$ respectively, table (4). The high linearity of the plots indicated by values of correlation coefficients ($R^2$) ($\geq$ 0.99) means that the adsorption kinetics between amidoxime chelating resin and heavy metals can be described using "pseudo-second-order adsorption kinetic model", moreover the good agreement between ($q_e$, Cal) and ($q_{e,}$ Exp), gives further evidence for the fitting of the adsorption data, that means the adsorption of heavy metals onto amidoxime chelating resin done through chemical interaction between adsorbent and adsorbate. [5, 72, 73]


A
t/qt (min.g/mg)
Time (min)
70 mg/L
50 mg/L
30 mg/L
0
1
2
3
4
5
6
0
20
40
60
80


B
t/qt (min.g/mg)
Time (min)
70 mg/L
50 mg/L
30 mg/L
0
1
2
3
4
5
0
20
40
60
80

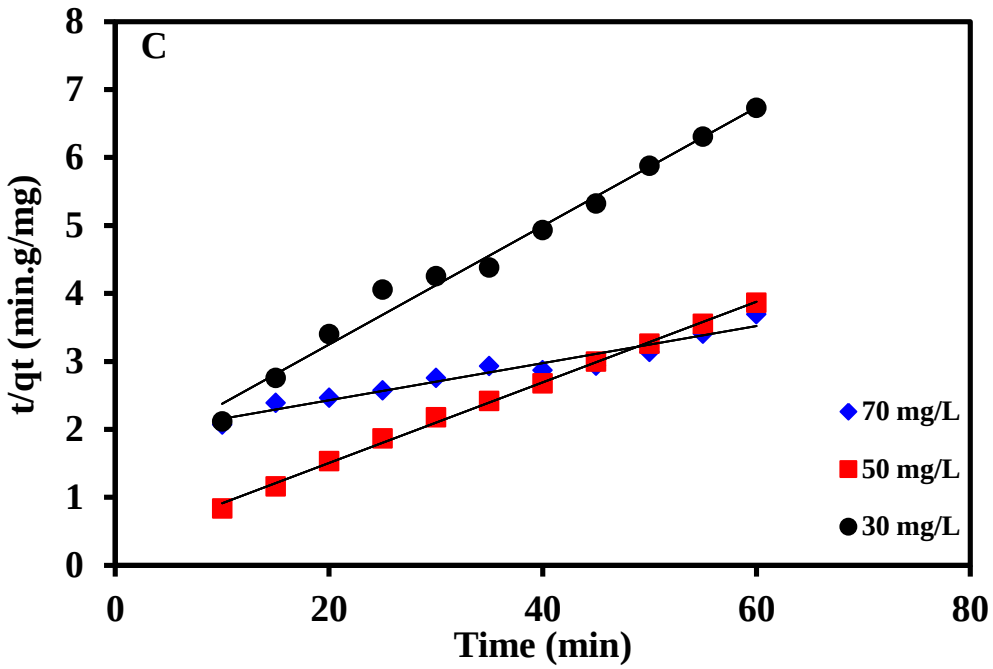


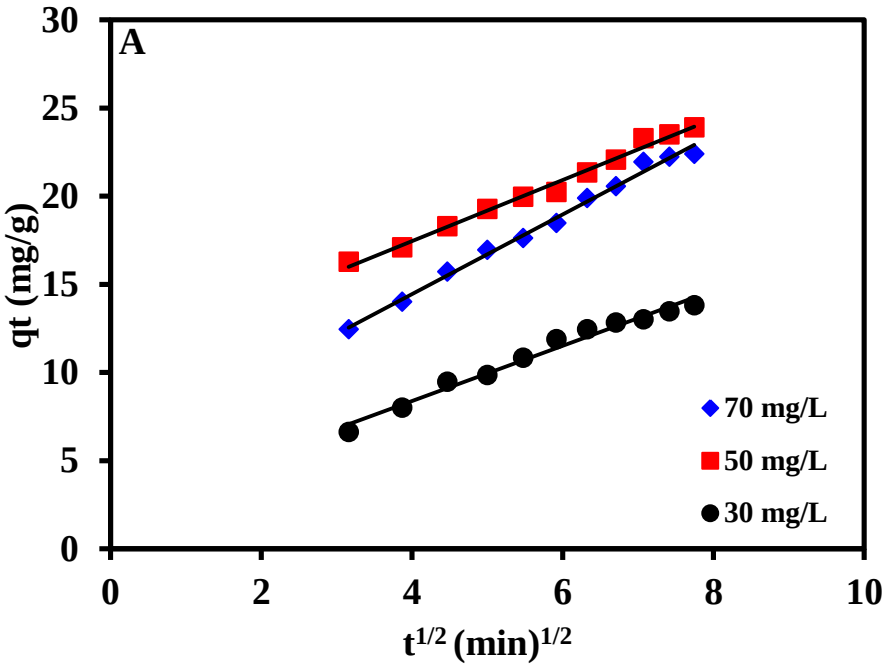

**Figure 33 Pseudo-second-order kinetic plot for adsorption of (A) Pb (II), (B) Cr (III), and (C) Cd (II) on amidoxime Chelating resin for different initial feed concentration at pH 5 and temperature 25 °C.**

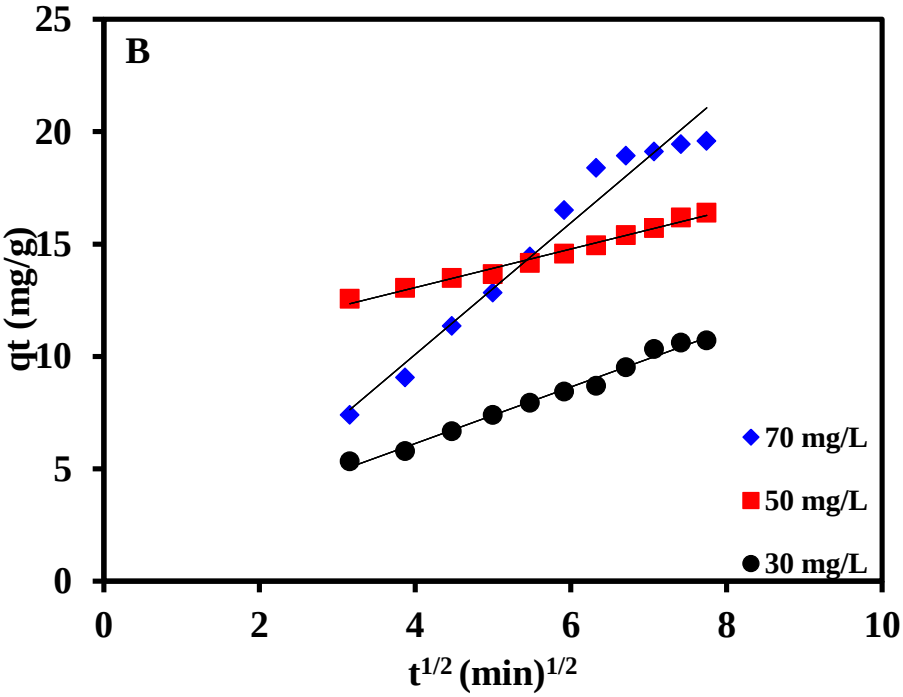
### 5.8.3 The intraparticle diffusion model

Adsorption mechanism and intra-particle diffusion rate determent step of lead (II), Cr (III) and Cd (II) onto chelating resin was identify using Weber and Morris model, the rate constant for intra- particle ($k_{id}$) can expressed as:

$$q_t = k_{id} t^{1/2} + C \qquad (5.8)$$

Fig. (34) demonstrate the plots of $q_t$ versus $t^{1/2}$ we can see clearly all lines for different concentrations don't pass through the point of origin, that indicate the difficulty of prediction the mechanism of the hole process and its seems to be very complex. [53, 56]


A
30
25
20
15
10
5
0
qt (mg/g)
0
2
4
6
8
10
t1/2 (min)1/2
70 mg/L
50 mg/L
30 mg/L


B
25
20
15
10
5
0
qt (mg/g)
0
2
4
6
8
10
t1/2 (min)1/2
70 mg/L
50 mg/L
30 mg/L

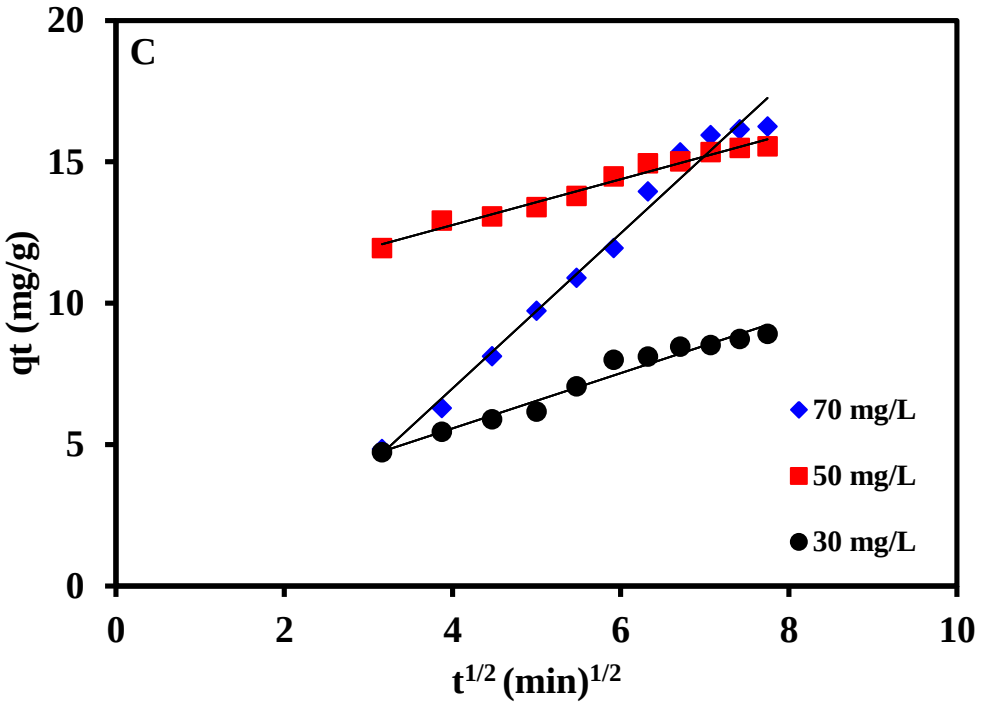



**Figure 34 Intraparticle diffusion kinetic plot for adsorption of (A) Pb (II), (B) Cr (III), and (C) Cd (II) on amidoxime Chelating resin for different initial feed concentration at pH 5 and temperature 25 °C.**

**Table 4 Kinetic constant parameters obtained for heavy metal adsorption on polyamidoxime resin.**

| Metal | | Pseudo-first order | | | | Pseudo-second order | | | Intraparticle diffusion model | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_i$(mg/L) | $q_e$exp(mg/g) | $K_1(10^{-3})(min^{-1})$ | $q_e$cal(mg/g) | $R^2$ | $K_2(^{10-2})$ (g/mgmin) | $q_e$ ,cal(mg/g) | *h* (g/min) | $R^2$ | $K_{id}$(mg/gmin) | C (mg/g) | $R^2$ |
| Pb(II) | 70 | 22.40 | 41.22 | 518.8 | 0.976 | 0.30 | 17.95 | 0.97 | 0.996 | 2.262 | 5.39 | 0.992 |
| | 50 | 23.90 | 32.70 | 226.01 | 0.976 | 0.40 | 27.03 | 2.91 | 0.992 | 1.733 | 10.52 | 0.990 |
| | 30 | 13.81 | 53.19 | 363.09 | 0.981 | 0.24 | 27.85 | 1.82 | 0.990 | 1.567 | 2.11 | 0.979 |
| Cr(III) | 70 | 19.58 | 62.87 | 1659.7 | 0.880 | 0.08 | 32.79 | 0.89 | 0.974 | 2.929 | 1.63 | 0.965 |
| | 50 | 16.39 | 33.85 | 111.88 | 0.994 | 0.93 | 17.64 | 2.89 | 0.995 | 0.856 | 9.64 | 0.986 |
| | 30 | 10.72 | 29.48 | 43.58 | 0.974 | 0.31 | 14.47 | 0.64 | 0.970 | 1.259 | 1.08 | 0.988 |
| Cd(II) | 70 | 16.24 | 45.14 | 832.60 | 0.937 | 0.399 | 36.49 | 0.53 | 0.947 | 2.745 | 3.99 | 0.983 |
| | 50 | 15.54 | 53.19 | 19.13 | 0.921 | 1.10 | 16.86 | 3.14 | 0.998 | 0.808 | 9.54 | 0.977 |
| | 30 | 8.92 | 51.82 | 72.31 | 0.924 | 0.503 | 11.48 | 0.66 | 0.986 | 0.977 | 1.66 | 0.967 |

## 5.9 Adsorption isotherm models

The adsorption efficiency of poly amidoxime chelating resin toward heavy metals was tested using some isotherm models, it describe the partition of adsorbate molecules at equilibrium between solid and liquid phase. "Langmuir and Freundlich adsorption isotherm models" were used to determine the adsorption capacity of amidoxime chelating resin towards lead (II), Cr (III) and Cd (II).

### 5.9.1 The Langmuir isotherm model

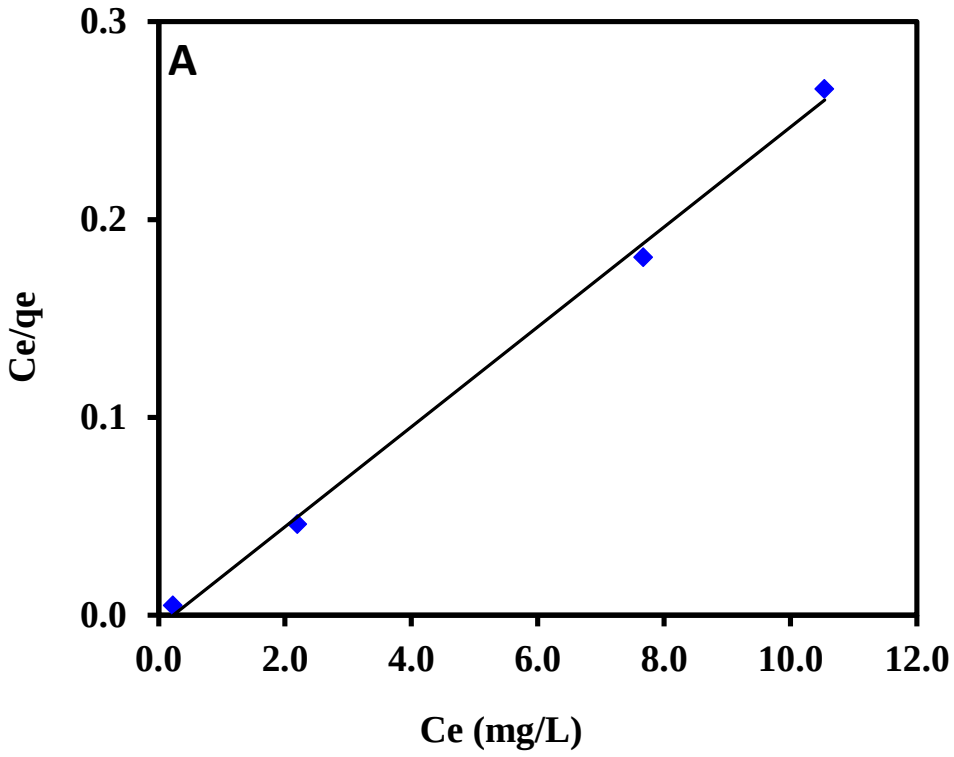
The Langmuir model assume that the monolayer adsorption process take place between adsorbate and adsorbent and the surface is homogenous with finite number of active sites when sites filled with adsorbate molecules there was no chance to further adsorption on this site and saturation point was achieved. [74] The linear equation expressed as:

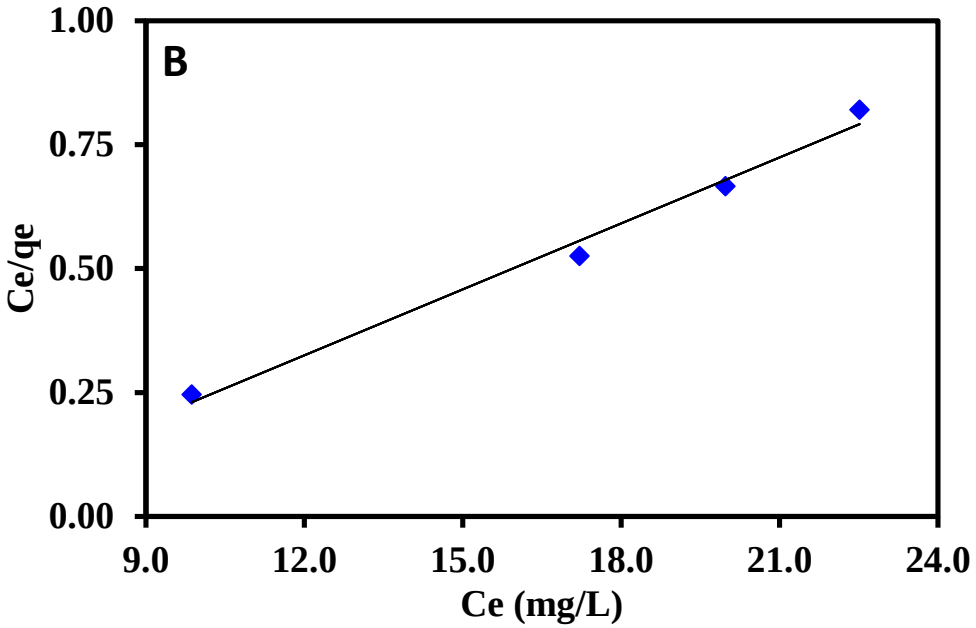
$$\frac{C_e}{q_e} = \frac{1}{k_l q_m} + \frac{C_e}{q_m} \qquad (5.9)$$

Where $C_e$ is the equilibrium concentration (mg/L) of metals in solution, qe is the amount of metal ions adsorbed (mg/g) at equilibrium, $K_L$ is Langmuir equilibrium constant (L/mg) and it's related to the affinity of adsorption sites and $q_m$ gives the maximum theoretical monolayer adsorption capacity (mg/g). The values of $q_m$ and $K_L$ (Table 5) were obtained from slope and intercept respectively of plots of $C_e/ q_e$ versus $C_e$ which demonstrated in Fig. (35). the linearity and high values of correlation coefficients ($R^2$) indicate that the Langmuir model can describe the adsorption process very well and confirm the formation of monolayer. Weber and Chakkravorti [62] defined the separation factor ($R_L$) as a characteristic dimensionless equilibrium parameter for Langmuir model and expressed as:

$$R_L = \frac{1}{1+K_L C_o} \quad (5.10)$$

The values of $R_L$ for each initial concentration (Table 5) was less than unity and greater than zero indicate the favourable adsorption of lead (II), Cr (III) and Cd (II) on poly amidoxime chelating resin. [53]





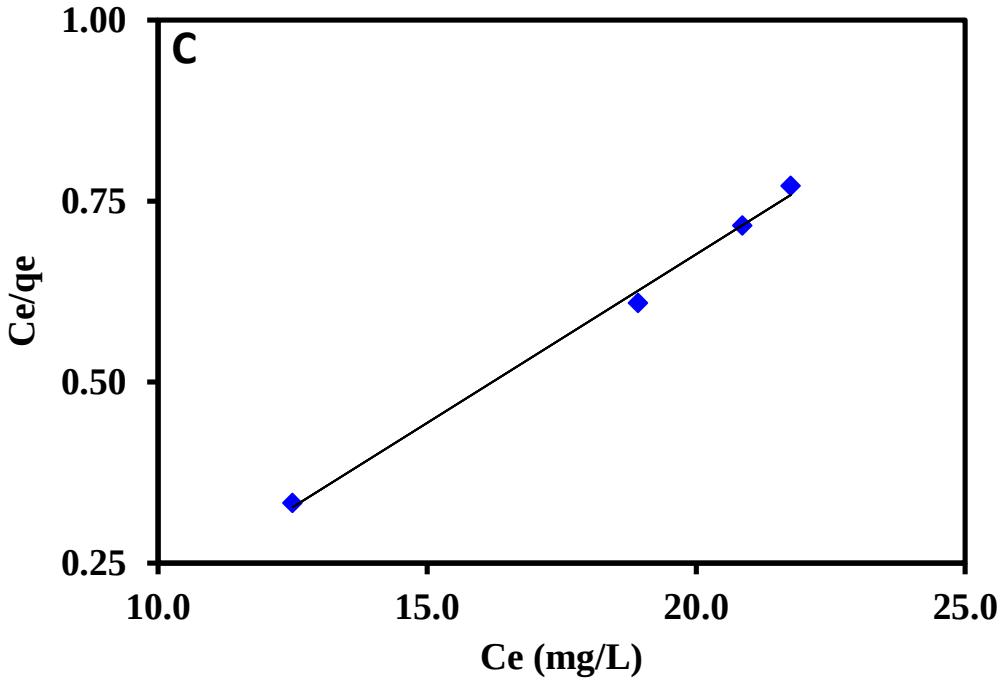



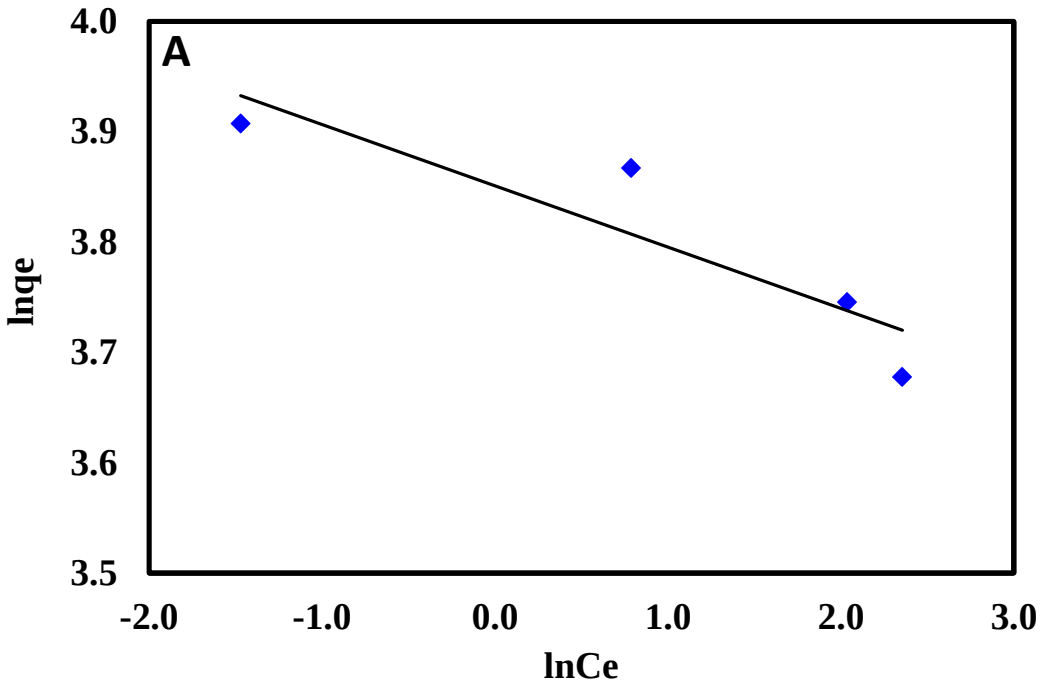

**Figure 35 Langmuir adsorption isotherms for adsorption of (A) Pb (II), (B) Cr (III), and (C) Cd (II) on amidoxime chelating resin, pH 5 and temperature 25 °C.**

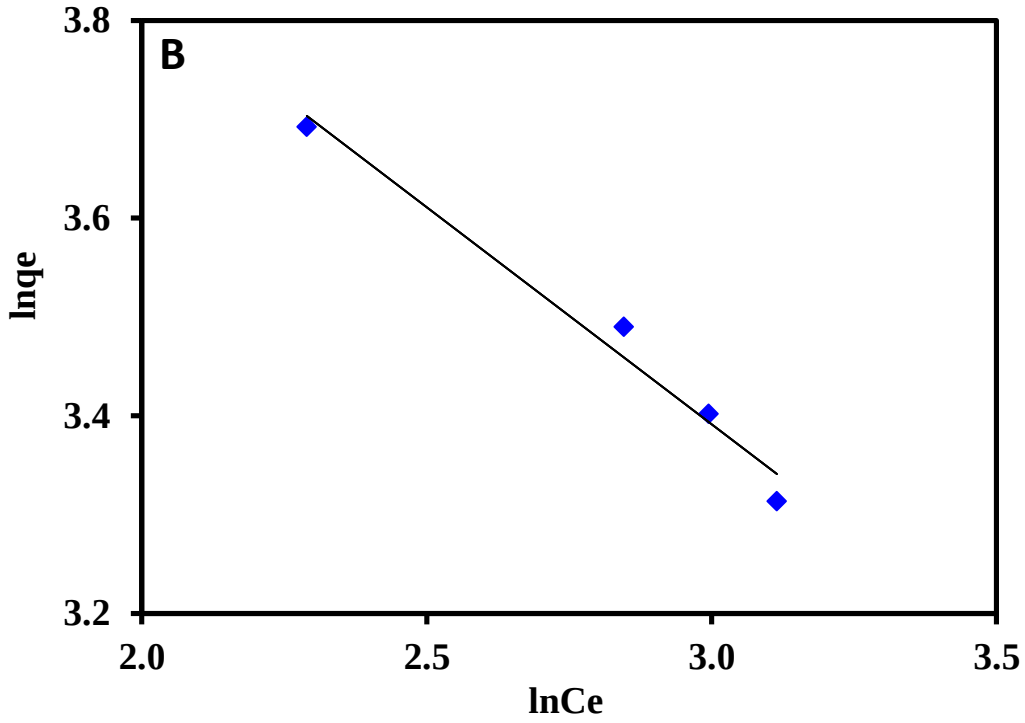
### 5.9.2 Freundlich isotherm model

The "Freundlich model" always used to describe adsorption in heterogeneous surface of an adsorbent. [75] Different initial concentrations of heavy metals under study were used with fixed dosage of amidoxime resin to obtain the equilibrium data, Freundlich isotherm model expressed as:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \qquad (5.11)$$

Where $K_f$ (mg/g) and n (g/L) are Freundlich adsorption constants, the plot of Lnqe against $\ln C_e$ Fig (36) gave straight lines and from slope and intercept of those lines we calculate the values of n and $K_f$ respectively (Table 5). Bad linearity and low values of correlation coefficient ($R^2$) indicate disagreement between equilibrium data and this model, values of n more than unit means favourable adsorption condition and lead (II), Cr (III) and Cd (II) are favourably adsorbed by prepared amidoxime resin. [64]


A
4.0
3.9
3.8
3.7
3.6
3.5
lnqe
-2.0
-1.0
0.0
1.0
2.0
3.0
lnCe


B
3.8
3.6
3.4
3.2
lnqe
2.0
2.5
3.0
3.5
lnCe

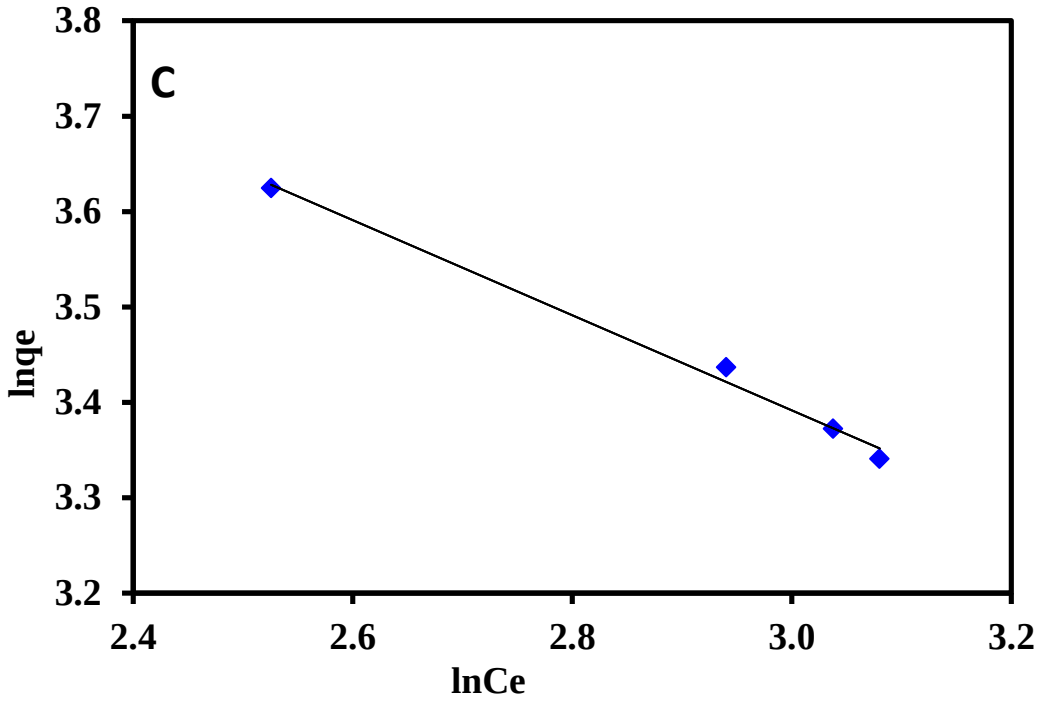



**Figure 36 Freundlich adsorption isotherms for adsorption of (A) Pb (II), (B) Cr (III), and (C) Cd (II) on amidoxime chelating resin, pH 5 and temperature 25 °C.**

**Table 5 Langmuir and Freundlich isotherm constants for Lead (II), Cr (III) and Cd (II) adsorption on amidoxime Chelating resin**

| Metal | T (k) | Langmuir isotherm constants | | | | Freundlich isotherm constants | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $q_m$ (mg/g) | $K_L$ (L/mg) | $R_L$ | $R^2$ | 1/n | n | $K_F$ | $R^2$ |
| **Pb(II)** | 298.16 | 39.68 | 4.340 | 0.005 | 0.9973 | 0.06 | 17.98 | 47.04 | 0.8208 |
| **Cr(III)** | 298.16 | 22.52 | 0.214 | 0.086 | 0.9876 | 0.44 | 2.28 | 110.87 | 0.9760 |
| **Cd(II)** | 298.16 | 21.50 | 0.183 | 0.098 | 0.9957 | 0.50 | 2.00 | 132.70 | 0.9925 |

# Conclusion

In this work grafted copolymerization was done for date palm wood fibre with some vinyl monomers using hydrogen peroxide as initiator and ammonium ferrous sulphate as catalyst, all parameters of grafting were studied to obtain the best percentage of grafting, this percentage depend on temperature of reaction, reaction period, amount of catalyst, concentration of initiator and volume of monomer. For methyl acrylate monomer the best temperature of reaction was 90 °C, reaction was done for 2 hours using 8ml of the methyl acrylate monomer, 0.15 mmol of catalyst and the concentration of hydrogen peroxide was 0.03M. On the other side the best yield of grafting using acrylonitrile monomer obtained with 8 ml of monomer, 0.306 mmol of catalyst, 0.03 M of hydrogen peroxide and reaction was done for 60 min at 75 °C. The grafted product was characterised using FT-IR and SEM techniques.Both grafted copolymers of MA and AN were treated with hydroxylamine to give poly-hydroxamic acid and poly-amidoxime chelating resins respectively. FT-IR technique used to confirm the process of conversion. The adsorption capacities of both resins towards heavy metal ions was studied using batch technique. The optimum pH of adsorption for both metals was found at range 5-6. Poly-hydroxamic acid resin showed better adsorption behaviour than poly-amidoxime resin in adsorption of lead (II), Cr (III) and Cd (II) from aqueous solution. By applying some kinetics models we found that the "pseudo-second-order model" describe the adsorption process very well for both resins. "Langmuir and Freundlich isotherms models" were applied for experimental data and it found obey Langmuir isotherm with best correlation coefficient above 0.99 for both resins.

## References:


1- http://www.newworldencyclopedia.org/entry/Date.

2- Tanweer Ahmad, Mohammad Danish, Mohammad Rafatullah, Arniza Ghazali, Othman Sulaiman, Rokiah Hashim and Mohamad Nasir Mohamad Ibrahim, The use of date palm as a potential adsorbent for wastewater treatment: a review, *Environmental Science and Pollution Research*, Volume 19, Issue 5, 1464-1484. 2012

3- Faraj A Abu-Ilaiwi, Mansor B Ahmad, Nor Azowa Ibrahim, Mohamad Zaki., Ab Rahman, Khairul Zaman Md Dahlan and Wan Md Zin Wan Yunus Optimized conditions for the grafting reaction of poly-(methyl acrylate) onto rubberwood fiber, *Polymer International* 53:386–391. 2004

4- Rajangam Vinodh, Rajangam Padmavathi and Dharmalingam Sangeetha, Separation of heavy metals from water samples using anion exchange polymers by adsorption process, *Desalination* Volume 267, Pages 267–276. 2011

5- Alma Rosa Netzahuatl-Muñoz, Flor de María Guillén-Jiménez, Benjamín Chávez-Gómez, Thelma Lilia Villegas-Garrido and Eliseo Cristiani-Urbina, Kinetic Study of the Effect of pH on Hexavalent and Trivalent Chromium Removal from Aqueous Solution by Cupressus lusitanica Bark, *Water, Air, & Soil Pollution*, Volume 223, Issue 2, pp 625-641. 2012

6- Nuri Ünlü and Mustafa Ersoz, Removal of heavy metal ions by using dithiocarbamated-sporopollenin, *Separation and Purification Technology*, Volume 52, Issue 3, Pages 461–469. 2007

7- Xiaoya Yuan, Bangshang Zhu, Gangsheng Tong,a Yue Sub and Xinyuan Zhuab, Wet-chemical synthesis of Mg-doped hydroxyapatite nanoparticles by step reaction and ion exchange processes, *Journal of Materials Chemistry B*, 1, 6551-6559. 2013

8- Mohammad Iqbal Lone, Zhen-li He, Peter J. Stoffella and Xiao-e Yang, Phytoremediation of heavy metal polluted soils and water: Progresses and perspectives, *Journal of Zhejiang University Sciences B*.; 9(3): 210–220. 2008

9- A. D. Sahasrabudhe, K. C. Mohite,.Sandeep Joshi, R. P. Thanedar, Mangesh Kashyap, and Ms. Shirish Ambegaonkar. *2nd International Conference on Waste Water Technology for Greening India*, ISSN- 2320- 5997. 2014

10- Ileana Cornelia Farcasanu, Mihaela Matache, Virgil Iordache, and Aurora Neagoe, Hyperaccummulation: *A Key to Heavy Metal Bioremediation, Soil Biology*, Chapter 13. 2012

11- Erika Mohanty and B. C. Singh,Graft copolymerization of methyl methacrylate onto jute fiber initiated by cerium (IV)–DMSO redox initiator system, *Journal of Applied Polymer Science*, Volume 69, Issue 13, pages 2569–2576. 1998

12- B. Focher, A. Marzetti1, E. Marsano, G. Conio, A. Tealdi, A. Cosani and M. Terbojevich, Regenerated and graft copolymer fibers from steam-exploded wheat straw: Characterization and properties, *Journal of Applied Polymer Science*, Volume 67, Issue 6, pages 961–974. 1998

13- J. Schurz, A bright future for cellulose, *Progress in Polymer Science* Volume 24, Issue 4, Pages 481–483. 1999

14- Yebang Tan, Liming Zhang and Zhuomei Li, Synthesis and characterization of new amphoteric graft copolymer of sodium carboxymethyl cellulose with acrylamide and

dimethylaminoethyl methylacrylate, *Journal of Applied Polymer Science*, Volume 69, Issue 5, pages 879–885. 1998

15- Niyazi Biçaka, David C Sherrington and B.Filiz Senkal, Graft copolymer of acrylamide onto cellulose as mercury selective sorbent, *Reactive and Functional Polymers*, Volume 41, Issues 1–3, Pages 69–76. 1999

16- P. Miretzky, A. Fernandez Cirelli, Hg (II) removal from water by chitosan and chitosan derivatives: A review, *Journal of Hazardous Materials*, Volume 167, Issues 1-3, 15 August, Pages 10-23. 2009

17- A.M.A. Nada, A.A. El-Gendy, S.H. Mohamed, Banana leaves as adsorbents for *removal of metal ions from waste water*, Carbohydrate Polymers 82, 1025–1030. (2010)

18- Ezzat M. Soliman, Salwa A. Ahmed, Aliaa A. Fadl, Reactivity of sugar cane bagasse as a natural solid phase extractor for selective removal of Fe(III) and heavy-metal ions from natural water samples, *Arabian Journal of Chemistry* 4, 63–70. 2011

19- Osvaldo Karnitz Júnior, Leandro Vinícius Alves Gurgel, Rossimiriam Pereira de Freitas, Laurent Frédéric Gil, Adsorption of Cu (II), Cd (II), and Pb (II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse chemically modified with EDTA dianhydride (EDTAD), *Carbohydrate Polymers*, 77, 643–650. 2009

20- Mohammad A. Al-Ghouti, Juiki Li, Yousef Salamh, Nasir Al-Laqtah, Gavin Walker, Mohammad N.M. Ahmad, Adsorption mechanisms of removing heavy metals and dyes from aqueous solution using date pits solid adsorbent, *Journal of Hazardous Materials* 176, 510–520. 2010

21- Salwa A. Ahmed, Batch and fixed-bed column techniques for removal of Cu (II) and Fe (III) using carbohydrate natural polymer modified complexing agents, *Carbohydrate Polymers*, 83, 1470–1478. 2011

22- Xiaomin Li, Yanru Tang, Xiuju Cao, Dandan Lu, Fang Luo, Wenjing Shao, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 317, 512–521. 2008

23- Liyuan Huang, Zhaoyang Ou, Thomas B. Boving, Julian Tyson, Baoshan Xing, Sorption of copper by chemically modified aspen wood fibers, *Chemosphere*,76, 1056–1061. 2009

24- Belala Z, Jeguirim M, Belhachemi M, Addoun F, Trouve G, Biosorption of copper from aqueous solutions by date stones and palm-trees waste. *Environmental Chemistry Letters*, 9, 65–69. 2011

25- F. Boudrahem, F. Aissani-Benissad, and A. Soualah , Adsorption of Lead (II) from Aqueous Solution by Using Leaves of Date Trees as an Adsorbent, *Journal of Chemical and Engineering Data*, 56, 1804–1812. (2011)

26- Paul Ocheje Ameh and Raphael Odoh, Iraqi Palm-date as Adsorbent for Removal of Pb(II) and Ni(II) Ions from Aqueous Solution, *International Journal of Modern Chemistry*. 4(1): 11-18. 2013

27- El-Hendawy A-NA The role of surface chemistry and solution pH on the removal of $Pb^{2+}$ and $Cd^{2+}$ ions via effective adsorbents from low-cost biomass, *Journal of Hazard Mater* 167:260–267. 2009

28- El Nemr A, Khaled A, Abdelwahab O, El-Sikaily, Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed. *Journal of Hazard Mater*, 152:263–275. 2008

29- Abdulkarim M, Al-Rub FA Adsorption of lead ions from aqueous solution onto activated carbon and chemically-modified activated carbon prepared from date pits. *Adsorption Science Technology,* 22:119–134. 2004

30- F. Bouhamed, Z. Elouear and J. Bouzid, Adsorptive removal of copper (II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Equilibrium, kinetics and thermodynamics, *Journal of the Taiwan Institute of Chemical Engineers*, 43,741–749. 2012

31- El-Said Ibrahim El-Shafey & Salma Muhammed Zahran Al-Kindy, Removal of $Cu^{2+}$ and $Ag^{+}$ from aqueous solution on a chemically-carbonized sorbent from date palm leaflets, *Environmental Technology*, 34:3, 395-406. 2013

32- Banat F, Al-Asheh S, Al-Rousan D, A Comparative study of copper and zinc ion adsorption on to activated and non-activated date-pits. *Adsorption Science Technology*, 20:319–335. 2002

33- Kang, S.Y., Lee, J.U., Moon, S.H., Kim, K.W., Competitive adsorption characteristics of $Co^{+2}$, $Ni^{+2}$, and $Cr^{+3}$ by IRN-77 cation exchange resin in synthesized wastewater. *Chemosphere*, 56, 141-147. 2004

34- Alyüz, B., Veli, S., Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. *Journal of Hazard Mater*, 167, 482-488. 2009

35- F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, *Journal of Environmental Management*, 92, 407-418. 2011

36- M. R. Lutfor, S. Sidik, W. M. Z. Wan Yunus, M. Z. A. Rhman, A. Mansor, M. J. Haron, Synthesis and Characterization of Poly-(hydroxamic acid) Chelating Resin from Poly-(methyl acrylate)-Grafted Sago Starch, *Journal of Applied Polymer Science*, Vol. 79, 1256–1264. 2000

37- F. Vernon and T. Shah, The Extraction of Uranium from seawater by Poly-(amidoxime)/poly-(hydroxamic acid) resins and fiber, *Reactive Polymers*, 1, 301-308. 1983

38- K Srinivasa Rao, PK Dash, D Sarangi, G Roy Chaudhury and VN Misra, Treatment of wastewater containing Pb and Fe using ion-exchange techniques, *Journal of Chemical Technology and Biotechnology*,80:892–898. 2005

39- K Srinivasa Rao, D Sarangi, PK Dash and G Roy Chaudhury, Preferential extraction of gallium from Bayer liquor using ion exchange chelating resin containing hydroxamic acid functional group, *Journal of Chemical Technology and Biotechnology*, 78:555–561. 2003

40- Faraj A. Abuilaiwi, Muataz Ali Atieh, Mansor B. Ahmad, Nor Azowa Ibrahim, Mohamad Zaki Ab. Rahman and Wan Md. Zin Wan Yunus, Preparation and Characterization of Polyamidoxime Chelating Resin from Rubberwood Fibre-g-Polyacrylonitrile**,** *Adsorption Science & Technology*, Vol. 27 No. 7**,**661-670. 2009

41- Pınar Akkas Kavak and Olgun Gu¨ven, Removal of Concentrated Heavy Metal Ions from Aqueous Solutions Using Polymers with Enriched Amidoxime Groups, *Journal of Applied Polymer Science*, Vol. 93, 1705–1710. 2004

42- M.J. Zohuriaan-Mehra, Pourjavadi and M. Salehi-Rad, Modified CMC. 2. Novel carboxymethylcellulose-based poly-(amidoxime) chelating resin with high metal sorption capacity, *Reactive & Functional Polymers*, 61, 23–31. 2004

43- Khalid Saeed, Sajjad Haider, Tae-Jin Oh and Soo-Young Park, Preparation of amidoxime-modified polyacrylonitrile (PAN-oxime) nanofibers and their applications to metal ions adsorption, *Journal of Membrane Science*, 322, 400–405. 2008

44- Baojiao Gao, Yuechao Gao, and Yanbin Li, Preparation and chelation adsorption property of composite chelating material poly-(amidoxime)/SiO2 towards heavy metal ions, *Chemical Engineering Journal* 158, 542–549. 2010

45- Nor Azowa Ibrahim, Wan Md Zin Wan Yunus, Faraj A. Abu-Ilaiwi, Mohd Zaki Ab Rahman, Mansor Bin Ahmad and Khairul Zaman M. Dahlan, Graft copolymerization of methyl methacrylate onto oil palm empty fruit bunch fiber using $H_2O_2/Fe^{2+}$ as an initiator, *Journal of Applied Polymer Science*, Volume 89, Issue 8, pages 2233–2238. 2003

46- Phiriyatorn Suwanmala, Kasinee Hemvichian, Hiroyuki Hoshina, Wannee Srinuttrakul and Noriaki Seko, Preparation of metal adsorbent from poly-(methyl acrylate)-grafted-cassava starch via gamma irradiation, *Radiation Physics and Chemistry*, Volume 81, Issue 8, Pages 982–985. 2012

47- S. S. Tripathy, S. Jena, S. B. Misra, N. P. Padhi and B. C. Singh, A study on graft copolymerization of methyl methacrylate onto jute fiber, *Journal of Applied Polymer Science*, Volume 30, Issue 4, pages 1399–1406. 1985

48- Lutfor Rahman, Sidik Silong, Wan Md Zin, M. Zaki Ab Rahman, Mansor Ahmad and Jelas Haron, Graft copolymerization of methyl acrylate onto sago starch using ceric ammonium nitrate as an initiator, *Journal of Applied Polymer Science*, Volume 76, Issue 4, pages 516–523. 2000

49- M.R. Lutfor, S. Sidik, W.M.Z. Wan Yunus, M.Z. Ab Rahman, A. Mansoor, H. Jelas, Preparation and swelling of polymeric absorbent containing hydroxamic acid group from polymer grafted sago starch, *Carbohydrate Polymers* Volume 45, Issue 1, Pages 95–100. 2001

50- M. R. Lutfor, S. Sidik, W. M. Z. Wan Yunus, M. Z. A. Rahman, A. Mansor and M. J. Haron, Synthesis and characterization of poly(hydroxamic acid) chelating resin from poly(methyl acrylate)-grafted sago starch, *Journal of Applied Polymer Science*, Volume 79, Issue 7, pages 1256–1264. 2001

51- P.Thilagavathy and T. Santhi, Adsorption of Cr (VI) Onto Low-Cost Adsorbent Developed from Acacia Nilotica Leaf Activated with Phosphoric Acid: Kinetic, Equilibrium Isotherm and Thermodynamic Studies, *International Journal of Science and Research*, Volume 3 Issue 5, pages 308-314. 2014

52- M. Ghasemi, Mu. Naushad, N. Ghasemi and Y. Khosravi-fard, a novel agricultural waste based adsorbent for the removal of Pb (II) from aqueous solution: Kinetics, equilibrium and thermodynamic studies, *Journal of Industrial and Engineering Chemistry*, Volume 20, Issue 2, Pages 454–461. 2014

53- Zeid A. ALOthman, Mu Naushad and Rahmat Ali, Kinetic, equilibrium isotherm and thermodynamic studies of Cr (VI) adsorption onto low-cost adsorbent developed

from peanut shell activated with phosphoric acid, *Environmental Science and Pollution Research* 20:3351–3365. 2013

54- Vinod Kumar Gupta, Imran Ali, Tawfik A. Saleh, M. N. Siddiqui and Shilpi Agarwal, Chromium removal from water activated carbon developed from waste rubber tires, *Environmental Science and Pollution Research*, Volume 20, Issue 3, pp 1261-1268. 2013

55- Mu. Naushad, Z.A. ALOthman and M.R. Khan, Removal of Malathion from aqueous solution using De-Acidite FF-IP resin and determination by UPLC–MS/MS: Equilibrium, kinetics and thermodynamics studies, *Talanta*, Volume 115, Pages 15–23. 2013

56- Sunil Kumar Yadava, Dhruv Kumar Singha and Shishir Sinha, dsorptive Removal of Hg (II) From Synthetic and Real Aqueous Solutions Using Modified Papaya Seed, *Journal of Dispersion Science and Technology*, pages 1-19. 2014

57- Ahlam M Farhan, Ammar H Al-Dujaili and Akl M Awwad, Equilibrium and kinetic studies of cadmium (II) and lead (II) ions biosorption onto Ficus carcia leaves, *International Journal of Industrial Chemistry*, 4:24. 2013

58- S.A. Odoemelam, C.U. Iroh and J.C. Igwe, Copper (II), Cadmium (II) and Lead (II) Adsorption Kinetics from Aqueous Metal Solutions Using Chemically Modified and Unmodified Cocoa Pod Husk (Theobroma cacao) Waste Biomass, *Research Journal of Applied Sciences*, Volume: 6, Issue: 1 Page No.: 44-52. 2011

59- K.S. Hui, C.Y.H. Chao and S.C. Kot, Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash, *Journal of Hazardous Materials*, Volume 127, Issues 1–3, Pages 89–101. 2005

60- Muataz Ali Atieh, Omer Yehya Bakather,Bassam Al-Tawbini, Alaadin A. Bukhari, Faraj Ahmad Abuilaiwi, and Mohamed B. Fettouhi, Effect of carboxylic functional group functionalized on carbon nanotubes surface on the removal of lead from water, *Bioinorganic Chemistry and Applications* ,Volume 2010, Article ID 603978, pages 1-9. 2010

61- Atul Kumar Kushwaha, Neha Gupta and M.C. Chattopadhyaya, Enhanced adsorption of methylene blue on modified silica gel: equilibrium, kinetic, and thermodynamic studies, *Desalination and Water Treatment*, 52, 4527–453. 2014

62- Weber, W. J., & Chakravarthi, R. K., Pore and solid diffusion modules for fixed bed adsorbent, *Journal of American Institute of Chemical Engineers*, 22, 228-238. 1974

63- Mu. Naushad, Anees A. Ansari, Zeid A. ALOthman and Jyoti Mittal, Synthesis and characterization of $YVO_4:Eu^{3+}$ nanoparticles: kinetics and isotherm studies for the removal of $Cd^{2+}$ metal ion, *Desalination and Water Treatment*, 1-8. 2014

64- Z.A. AL-Othman, R. Ali and Mu. Naushad, Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies, *Chemical Engineering Journal* Volume 184, Pages 238–247. 2012

65- S.A. Abdel-Hafiz, Potassium permanganate/thioureadioxide redox system-induced grafting of methacrylic acid onto loomstate cotton fabric, *Journal of Applied Polymer Science*, Volume 58, Issue 11, pages 2005–2011. 2005

66- S. Mishra, M. Misra, S. S. Tripathy, S. K. Nayak and A. K. Mohanty, Graft Copolymerization of Acrylonitrile on Chemically Modified Sisal Fibers,

*Macromolecular Materials and Engineering*, Volume 286, Issue 2, pages 107–113. 2001

67- Ibrahim H. Mondal, Grafting of Methyl Acrylate and Methyl Methacrylate onto Jute fiber: Physico-Chemical Characteristics of the Grafted Jute, *Journal of Engineered Fibers and Fabrics*, Volume 8, Issue 3, 42-50. 2013

68- Sibendu Moharana and S. S. Tripathy, Chemical Modification of Jute Fibers. II: A Study on the $Fe^{2+}$/ $H_2O_2$-Initiated Graft Copolymerization of Methyl Methacrylate, Acrylonitrile, and Acrylamide onto Jute Fibers, *Journal of Applied Polymer Science*, Vol. 42, 1001-1008. 1991

69- Suresh K. Sahni and Jan Reedijk, Coordination chemistry of chelating resins and ion exchangers, *Coordination Chemistry Reviews*, Volume 59, Pages 1–139. 1984

70- Y. El Mouzdahir, A. Elmchaouri, R. Mahboub, A. ElAnssari, A. Gilc, S.A. Korili and M.A. Vicente, Interaction of stevensite with $Cd^{2+}$ and $Pb^{2+}$ in aqueous dispersions, *Applied Clay Science* Volume 35, Issues 1–2, Pages 47–58. 2007

71- Hanan S. Ibrahim, Ahmed A. El-Kady, Nabila S. Ammar, Ladda Meesuk, Pornsawat Wathanakul, and Mosaad A. Abdel-Wahhab, Application of Isotherm and Kinetic Models for the Removal of Lead Ions from Aqueous Solutions, *Journal of Environmental Engineering*, 139:349-357. 2013

72- B. Karagozoglu, M. Tasdemir, E. Demirbas, M. Kobya, The adsorption of basic dye (Astrazon Blue FGRL) from aqueous solutions onto sepiolite, fly ash and apricot shell activated carbon: Kinetic and equilibrium studies, *Journal of Hazardous Materials*, Volume 147, Issues 1–2, Pages 297–306. 2007

73- A.M. El-Kamash, B. El-Gammal, A.A. El-Sayed, Preparation and evaluation of cerium (IV) tungstate powder as inorganic exchanger in sorption of cobalt and europium ions from aqueous solutions, *Journal of Hazardous Materials* Volume 141, Issue 3, Pages 719–728. 2007

74- Langmuir, I., The Constitution and fundamental properties of solids and liquids. Part I. solids. *Journal of the American Chemical Society*, 38(11), 2221-2295. 1916

75- Freundlich, H., Uber die adsorption in losungen [Adsorption in solution]" *Zeitschrift für Physikalische Chemie*, 57: 384-370. 1906

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